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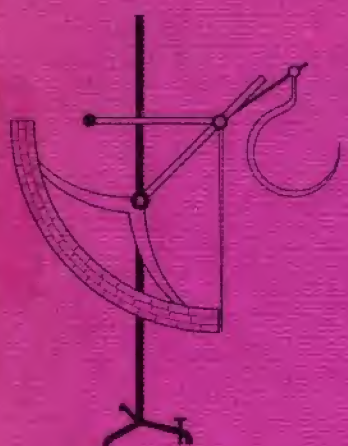

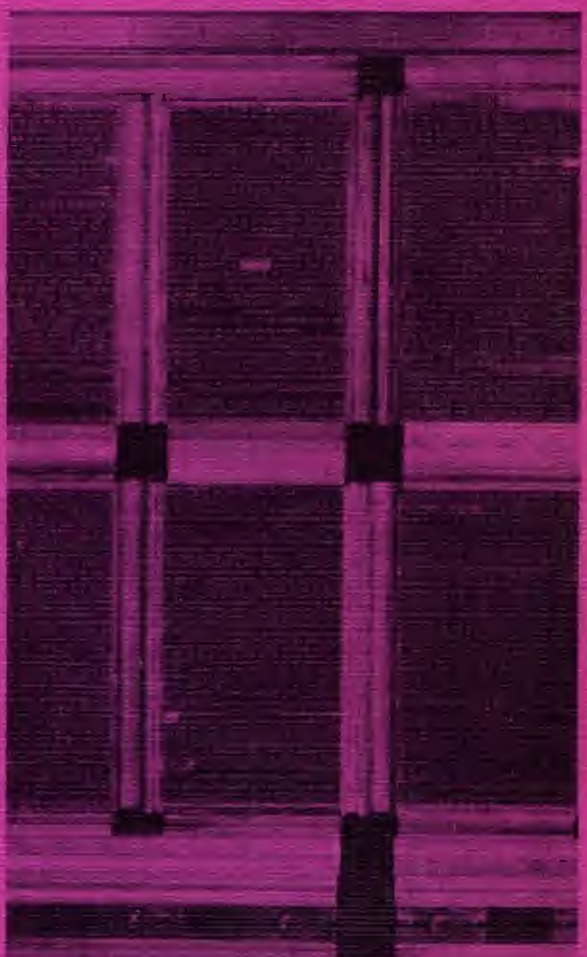

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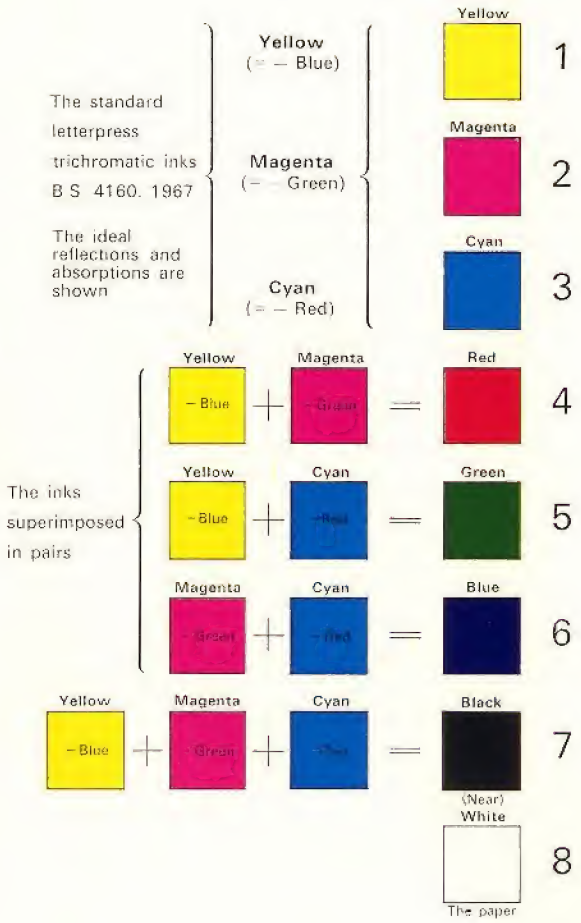

PRINTING: BASIC SCIENCE

BY

CHARLES C. AMMONDS,

B.SC.(LONDON), ARIC, FRPS, FIOP

1966

PERGAMON PRESS

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PERGAMON PRESS

PERGAMON PRESS LTD.

OXFORD · LONDON · EDINBURGH
NEW YORK · TORONTO · SYDNEY

First Edition 1970

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Library of Congress Catalog Card No. 71–89611

Printed in Great Britain by A. Wheaton & Co., Exeter

HARRIS COLLEGE
PRESTON
502·4 6862 AMM
25475
FOY 3.70
e 35

08 006408 6

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Preface

IT HAS been said so often that it has become almost a bore, but printing really is both an ancient craft and a pioneer machine industry; with these roots in the past it has been, or so it appears, rather reluctant to keep up with the glittering technologies which illuminate our age.

Nevertheless, there are clear signs of change.

This book is, first, an attempt to set down as fully as possible within its limits the scientific bases of this complex industry; it is, secondly, an attempt to present material to meet the requirements of the syllabuses of the printing subjects of the City and Guilds of London Institute and similar examination authorities and to provide at least an introduction to the lower levels of the certificate courses of the Institute of Printing.

A little on the plan of the book seems appropriate at this point. There are five parts and it is hoped that this division will be accepted as rational. The opening is devoted to a brief survey of mathematics which is carried a little beyond that required by the syllabuses mentioned above. It will not occasion surprise if the inclusion of the subject at all is felt by some to be unnecessary, but it is not possible to grasp the meaning of pH without understanding common logarithms or to follow the optical formulae and the transpositions of the components of Ohm's law without knowledge of simple algebraic equations.

It will be seen that whenever worked examples are really needed to illustrate a principle the numerical quantities are always simple since it is felt that formulae are often difficult enough to follow without the burden of complex arithmetic.

Very little originality is possible in a work of this character; all that may be claimed, perhaps, is some novelty here and there in the manner of presentation.

There are inevitably very many references to PIRA, the Printing Industry Research Association, which will remain more familiar to many as PATRA. The debt to that Association and to the very many former colleagues in the colleges and in the industry is here gratefully acknowledged.

Sutton, Surrey C. C. A.

Part I

Mathematics and Measurement

CHAPTER 1

Mathematics

Introduction. Mathematics is the most profound of the sciences, or, as many would have it, of the arts; it is held to be the greatest manifestation of the intellect, and there are those who believe that the riddle of the universe will be solved as its frontiers are advanced.

There can be no hesitation on the importance of mathematics to the physical sciences and to technology; all public examining authorities concerned with the latter include the subject in the syllabuses.

Mathematics falls conveniently into several divisions, but these are not as isolated as they may appear to be at the earlier levels. These divisions are:

(a) *Arithmetic* which deals primarily with the manipulation of numbers.
(b) *Algebra* is concerned principally with symbolic expression.
(c) *Geometry* is the study of the qualities of lines, plane forms, and solid figures related to space.
(d) *Trigonometry* is devoted to numerical applications of geometry and particularly to the properties of triangles.

The matter below is intended to be introductory only or it may be regarded as indicating subjects for revision; for more complete information the reader is referred to the many excellent textbooks from which a selection may be made.

However, additional material is included where it is necessary to explain certain principles in physics and chemistry.

ARITHMETIC

Numbers

The denary or decimal system of numbers is in ordinary use everywhere; the root or radix is 10 and this is solely because man has ten fingers—these still serve as accounting apparatus. It would, indeed, have been a much more efficient system if there were six fingers on each hand since the result would have been the duodenary or duodecimal scale, the radix of which is divisible by 2, 3, 4, and 6; 10 is divisible by 2 and 5 only.

In the normal scale of notation 10 represents the radix, and the scale proceeds in steps marked by powers of 10.

The binary scale has only two digits—0 and 1, and as a consequence of this simplicity it is in general use for computers; a common form of the system is compared with the denary scale (Table 1.1).

Number symbols. The Arabic numerals, introduced into Europe in the Middle Ages, are of Indian origin. Although they did not come into normal use until the invention of printing, they have displaced all their predecessors; it is, indeed, a matter for speculation how the Romans managed any arithmetic at all.

Vulgar Fractions

(It is assumed that the reader is versed in the basic processes of addition, subtraction, multiplication, and division of whole numbers.) A vulgar fraction is defined as a quantity normally less than unity which is expressed by a "numerator" above and a "denominator" below a line.

Addition and subtraction. First convert all the denominators to the same value; if numerator and denominator are multiplied (or divided) by the same number the value of the fraction is unaltered:

$$\text{(a)}\quad \frac{1}{2}+\frac{3}{4}+\frac{4}{5} = \frac{10}{20}+\frac{15}{20}+\frac{16}{20} = \frac{41}{20} = 2\frac{1}{20}.$$

$$\text{(b)}\quad \frac{5}{6}-\frac{4}{5} = \frac{25}{30}-\frac{24}{30} = \frac{1}{30}.$$

TABLE 1.1

System	Radix												
Binary	2	1	10 (2^1)	11	100 (2^2)	101	110	111	1000 (2^3)	1001	1010	10000 (2^4)	
Denary	10	1	2	3	4	5	6	7	8	9	10 (10^1)	16	100 (10^2)

(c) $\frac{5}{8}+\frac{1}{2}-\frac{3}{5} = \frac{25+20-24}{40} = \frac{21}{40}$.

When whole numbers are present, put the mixed fractions into the form of improper fractions:

$$1\frac{3}{4}+2\frac{2}{3} = \frac{7}{4}+\frac{8}{3} = \frac{21+32}{12} = \frac{53}{12} = 4\frac{5}{12}.$$

Multiplication. Basically this is done by multiplying the numerators together and the denominators together. The process is simplified, where possible, by cancelling, i.e. dividing numerators and denominators by common factors.

(a) $\frac{\cancel{3}}{\cancel{16}_{8}} \times \frac{\cancel{2}}{\cancel{9}_{\cancel{3}}} \times \frac{\cancel{3}}{5} = \frac{1}{40}$

(b) $3\frac{1}{4} \times 1\frac{1}{39} = \frac{\cancel{13}}{\cancel{4}} \times \frac{\overset{10}{\cancel{40}}}{\cancel{39}_{3}} = \frac{10}{3} = 3\frac{1}{3}$.

Division. Invert the divisor and multiply; again simplify by cancelling:

$$\frac{4}{15} \div \frac{8}{9} = \frac{\cancel{4}}{\cancel{15}_{5}} \times \frac{\overset{3}{\cancel{9}}}{\cancel{8}_{2}} = \frac{3}{10}.$$

With mixed fractions again convert to improper fractions.

$$3\frac{1}{15} \div \frac{23}{30} = \frac{\overset{2}{\cancel{46}}}{\cancel{15}} \times \frac{\overset{2}{\cancel{30}}}{\cancel{23}} = 4.$$

Add, subtract, multiply, divide. First, work out between brackets; then multiply and divide—note that denominator is divisor of numerator:

$$\frac{\left(\frac{5}{6}+\frac{2}{3}\right) \times \frac{2}{5}}{\left(\frac{3}{4}-\frac{2}{3}\right) \div \frac{5}{6}} = \frac{\frac{3}{\cancel{2}} \times \frac{\cancel{2}}{5}}{\frac{1}{\cancel{12}_{2}} \times \frac{\cancel{6}}{5}} = \frac{\frac{3}{5}}{\frac{1}{10}} = \frac{3}{\cancel{5}} \times \frac{\overset{2}{\cancel{10}}}{1} = 6.$$

Decimal Fractions

These are a rational application of the denary scale of notation. The number 7832·564 means

Thousands	Hundreds	Tens	Units		Tenths	Hundredths	Thousandths
7	8	3	2	•	5	6	4

The decimal separates the multiples of 10 from the submultiples.

Addition and subtraction. The ordinary processes of arithmetic are applied; where integers and fractions are involved the decimal points must be vertically in line.

In setting down a fractional quantity it is desirable to write a zero to the left of the point: 0·2345.

A weakness of the system is the existence of infinitely recurring fractions; $\frac{1}{3} = 0{\cdot}333333333\ldots$ written $0{\cdot}3\dot{}$

Multiplication. Multiply in the arithmetical manner and mark off sum of decimal places from the right:

(a) $0{\cdot}48 \times 0{\cdot}7$

$$\begin{array}{r} 0{\cdot}48 \\ 0{\cdot}7 \\ \hline 336 \end{array}$$

(3 decimal places) = 0·336.

(b) $22{\cdot}66 \times 0{\cdot}06$

$$\begin{array}{r} 22{\cdot}66 \\ 0{\cdot}06 \\ \hline 13596 \end{array}$$

(4 decimal places) = 1·3596.

Division. There are several methods of division; probably the simplest is to convert both divisor and dividend into whole numbers by moving the decimal point an equal number of places to the left (since this is equivalent to multiplying each by the same value the relation is unaltered). Division is carried out in the usual manner; when whole number division ceases, the decimal point is put in:

$28{\cdot}59 \div 0{\cdot}6 = 2859 \div 60$ (a shift of two places).

$$\begin{array}{l} 60\,)2859(\,47{\cdot}65 \\ \quad 240 \\ \quad \overline{459} \\ \quad\ 420 \\ \quad \overline{390} \\ \quad\ 360 \\ \quad \overline{300} \\ \quad\ 300 \\ \quad \overline{} \end{array}$$

In practice, in other than the simplest cases, multiplication and division of fractions as well as of complex whole numbers is carried out by the use of logarithms (see below).

Average. If the sum of several quantities is divided by the number of separate quantities the result is the average of those quantities:

(a) The average of 3, 5, 6, 8, 9, and 11 is $42 \div 6 = 7$.
(b) The average of $0 \cdot 25$, $0 \cdot 5$, and $0 \cdot 126$ is $0 \cdot 876 \div 3 = 0 \cdot 292$.

Arithmetic mean. A mean is a term equidistant from two other terms although it is very often used in the same sense as average:

(a) The mean of 13 and 17 is 15.
(b) The mean of $\frac{3}{16}$ ($\frac{30}{160}$) and $\frac{9}{10}$ ($\frac{144}{160}$) is $\frac{87}{160}$.

Ratio and proportion. Ratio is sometimes used to describe the link between two quantities; the ratio between 9 in. and 2 ft 3 in. (27 in.) may be stated as 1 : 3. More usually ratio is regarded as the equivalent of proportion which is defined as the numerical relationship between any number of quantities:

(a) Divide 144 in the ratio 3 : 4 : 5. The sum of the ratios is 12; therefore the result of division is

$$\frac{3}{12}(144), \frac{4}{12}(144), \frac{5}{12}(144); \text{ i.e. } 36, 48, 60.$$

(b) The sides of a triangle are in the proportion 2 : 3 : 7; the shortest side is 8 cm. Calculate the remaining sides.

One side is $\frac{3}{2}(8)$ the other is $\frac{7}{2}(8)$, i.e. 12 cm and 28 cm.

Percentage. Percentage is a means of expressing different ratios or proportions in the same terms, i.e. hundredths, to afford a basis for comparison. One-half may be expressed as $\frac{50}{100}$ or 50 per cent; $\frac{3}{4}$ as 75 per cent.

(a) Three different operatives produce faulty work: (i) 15 per run of 1000, (ii) 16 per 1250, (iii) 17 per 1500. Express the inefficiency as percentages:

$$\text{(i) } \frac{15}{1000} \times 100, \quad \text{(ii) } \frac{16}{1250} \times 100, \quad \text{(iii) } \frac{17}{1500} \times 100; \text{ i.e.}$$

(i) 1·5 per cent (ii) 1·28 per cent, (iii) 1·133 per cent.

(b) A printing metal contains 10 per cent tin, 15 per cent antimony, and the remainder is lead. Calculate the weight of each component in 650 kg of the alloy:

(i) $\frac{10}{100}$ 650, (ii) $\frac{15}{100}$ 650, (iii) $\frac{75}{100}$ 650; i.e.

(i) tin 65 kg, (ii) antimony 97·5 kg, and (iii) lead 487·5 kg.

ALGEBRA

Symbols and conventions. While this branch of mathematics is chiefly concerned with generalizations expressed symbolically, numbers may also be involved; there are many conventions which differ considerably from those of arithmetic:

(a) Quantities are positive or negative; the former may or may not be preceded by the positive sign but the latter must always be indicated by the appropriate sign.

(b) The negative sign should not be regarded necessarily as standing for subtract: $a - b$ also means $a + (-b)$ and it could equally have been written $-b + a$.

(c) It is not necessary to put down the sign for multiply: $a \times b$ and $3 \times x$ are usually written ab and $3x$.

(d) Multiplication or division of a positive quantity by a positive gives a positive: $a \times b = ab$ and $a \div b = a/b$.

(e) Multiplication or division of a negative quantity by a negative gives a posative $(-a) \times (-b) = ab$ and $(-a) \div (-b) = a/b$.

(f) Multiplication or division of a negative quantity by a positive, or a positive quantity by a negative, gives a negative: $(-a) \times b = -ab$ and $a \times (-b) = -ab$; $(-a) \div b = -a/b$ and $a \div (-b) = -a/b$.

Addition. This is carried out as in arithmetic, but see (b) above.

$$\begin{array}{r} 3a + 4b - 5c \\ -2a - 3b + 4c \\ \hline a + b - c \end{array} \qquad \begin{array}{r} -10x + 9y - 8z \\ 11x - 8y + 9z \\ \hline x + y + z \end{array}$$

Subtraction. To subtract the lower from the upper line, reverse the signs of the lower and add.

$$\begin{array}{r} 3a + 4b - 5c \\ -2a - 3b + 4c \\ \hline 5a + 7b - 9c \end{array} \qquad \begin{array}{r} -10x + 9y - 8z \\ 11x - 8y + 9z \\ \hline -21x + 17y - 17z \end{array}$$

Indices. The raising of a quantity to a 'power', i.e. to multiply it by itself, is indicated by an 'index' placed to the upper right of the symbol:

a^2 (a squared) $= a \times a$; b^3 (b cubed) $= b \times b \times b$; c^4 (c to the power of 4 or to the fourth) $= c \times c \times c \times c$.

Manipulation of indices.

(a) To multiply similar quantities raised to powers add the indices: $x^3 \times x^2 = (x \times x \times x) \times (x \times x) = x^{3+2} = x^5$.

(b) To divide similar quantities raised to powers subtract the indices: $x^5 \div x^2 = \dfrac{x \times x \times x \times x \times x}{x \times x} = x^{5-2} = x^3$.

(c) To give a meaning to a negative index:

$x^2 \div x^6$ [by (b)] $= x^{2-6} = x^{-4}$; but $x^2 \div x^6$ may be written:

$\dfrac{\cancel{x} \times \cancel{x}}{\cancel{x} \times \cancel{x} \times x \times x \times x \times x} = \dfrac{1}{x^4}$; therefore $x^{-4} = \dfrac{1}{x^4}$.

(d) To give a meaning to x^1 and x^{-1}:

$x^3 \div x^2 = x^{3-2} = \dfrac{\cancel{x} \times \cancel{x} \times x}{\cancel{x} \times \cancel{x}} = x = x^1$; $x^2 \div x^3 = x^{-1} = \dfrac{1}{x}$

[see (c)].

(e) To give a meaning to x^0:

$x^3 \div x^3 = x^{3-3} = x^0$; but $\dfrac{x^3}{x^3} = 1$; *thus any quantity to the power of zero* $= 1$.

Roots. A root of a number is that quantity which, multiplied by itself 2, 3, 4, . . . times, gives that number; thus the square root of 4, i.e. ($\sqrt{4}$), the cube root of 8, i.e. ($\sqrt[3]{8}$), and the fourth root of 16, i.e. ($\sqrt[4]{16}$), all equal 2. While roots are usually expressed by the radix they may also be stated as powers with fractional indices, and they may be subjected to the processes above:

$\sqrt{a} = a^{\frac{1}{2}}$: $\sqrt[3]{a} = a^{\frac{1}{3}}$: $a^{\frac{1}{2}} \times a^{\frac{1}{2}} = a^{\frac{1}{2}+\frac{1}{2}} = a^{\frac{2}{2}}$: $a^{\frac{1}{2}} \div a^{\frac{1}{2}} = a^{\frac{1}{2}-\frac{1}{2}} = a^{\frac{0}{2}}$.

LOGARITHMS

Logarithms and indices. Applying the matter above to numbers:

$8 \times 4 = 2^3 \times 2^2 = 2^{3+2} = 2^5 = 32$

$64 \div 4 = 2^6 \div 2^2 = 2^{6-2} = 2^4 = 16$.

Any number may be expressed as a power of any base; the index of the power is the logarithm of the given number to the given base. From the examples above:

Since $2^3 = 8$, then 3 is the log of 8 to base 2:

Since $2^6 = 64$, then 6 is the log of 64 to base 2:

Common logarithms. The most convenient base is 10 and the index of a power to this base of a number is its 'common logarithm'. An advantage of this system is that the steps of the denary scale are indicated by a simple sequence of numerals (Table 1.2).

A logarithm is in two parts—a whole number which may be negative or positive, and a decimal fraction which is positive. The former is the 'characteristic' or 'index'; the latter is the 'mantissa'. The tables of logarithms give the mantissa of a number sequence irrespective of the position of a decimal point; the characteristic is found by inspection: thus the mantissa of the sequence 3456 is ·5386 (the zero to the left is deliberately omitted); the characteristic of a whole number (with or without a fraction) is one less than the digits to the left of the decimal point, while that of a fraction is one more than the zeros to the right of the point (see Table 1.2). Therefore, using the sequence and its mantissa already set down (Table 1.3):

TABLE 1.2

Number	10,000	1000	100	10	1	0·1	0·01	0·001	0·0001
Power	10^4	10^3	10^2	10^1	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}
Log	4	3	2	1	0	−1	−2	−3	−4

Note that in practice the negative sign is placed above the characteristic (see text).

TABLE 1.3

Number	3456·0	345·6	34·56	3·456	0·3456	0·03486	0·003486
Log	3·5386	2·5386	1·5386	0·5386	$\bar{1}$·5386	$\bar{2}$·5386	$\bar{3}$·5386

The negative sign of the characteristic is placed above the numeral (bar 1, bar 2, etc.) to indicate that it alone is negative.

The process of multiplication by the use of logarithms is carried out as shown in the matter above on indices—find the logarithms and add; refer the result to the tables of antilogarithms; here a number sequence only appears, a decimal point or zeros to follow that point being inserted according to the characteristic. The practice for division is similar except that the log of the divisor is subtracted from that of the dividend.

Multiply 51·56 by 0·02894 (add logs; 1 is carried over from the fractions and to the left of the point, the addition is $1 + (-2) + 1 = 0$). The antilog is 1492; since the characteristic is 0 the result is 1·492.

No	Log
51·56	1·7123
0·02894	$\bar{2}$·4615
	0·1738

Divide 51·56 by 0·02894 (subtract logs; to the left of the point the subtraction becomes $1 - (-2)$ or $1 + 2 = 3$). The antilog is 1780; since the characteristic is 3 the result is 1780·0.

No	Log
51·56	1·7123
0·02894	$\bar{2}$·4615
	3·2506

The examples are from four-figure tables; these serve most purposes, but there may be small inaccuracies in the final digit; for more critical work, five- and seven-figure tables are available.

The majority of books of mathematical tables contain full instructions on the use of logarithms.

Formulae. A formula expresses a relationship between its

components, usually symbolically and frequently as an equation in which one component, the subject, is stated in terms of the others. It is often required that the expression should be set down in a different form; this may be achieved by transposition of the components, but the character of the terms must be changed from positive to negative or from divisor to factor or to the converse of each, as appropriate:

(a) Given that $a + b = c - d$, then $a = c - d - b$ or $b = c - d - a$.
(b) Given that $a/b = cd$, then $a = bcd$ and $d = a/(bc)$.
(c) Make x the subject of $y = mx + c$; $mx = y - c$ and $x = (y - c)/m$.

Simple equations. In a simple equation, an unknown of the first degree, usually in x, is required. The rules on transposition given above are applied, and it is normal practice to collect the numerical quantities on the right-hand side.

Solve the equations:

(a) $2x + 3 = 11$; $2x = 11 - 3$; $2x = 8$; $x = \frac{8}{2}$ $\therefore x = 4$.
(b) $4x - 3 = 2x + 5$; $4x - 2x = 5 + 3$; $2x = 8$ $\therefore x = 4$.
(c) $\frac{3}{4}x + 2 = 5$; $\frac{3}{4}x = 3$; $3x = 3 \times 4$; $3x = 12$ $\therefore x = 4$.

Quadratic equations. A quadratic is an equation in which the unknown is of the second degree. There are many methods but, in its simplest form, a quadratic is solved by resolution into factors; it is necessary to note that every quadratic equation has two 'roots' even if they are equal:

(a) $x^2 - 4 = 0$; $x^2 = 4$. $x = \pm 2$ since (2^2) and $(-2^2) = 4$.
(b) $x^2 - 2x + 1 = 0$; the factors are $(x - 1)$ $(x - 1)$ and when $x = 1$ in either bracket the expression is zero. $x = 1, 1$.
(c) $x^2 - 3x + 2 = 0$; factors $(x - 2)$ $(x - 1)$. $x = 2, 1$.
(d) $x^2 + 2x - 3 = 0$; factors $(x + 3)$ $(x - 1)$. $x = -3, +1$.

The factors are found in the above by trial and error: practice eases this apparent difficulty.

GEOMETRY

Introduction. Apart from simple arithmetic at the finger-tips geometry is held to be the earliest branch of mathematics. It involves the study of axioms—i.e. self-evident truths—and theorems—i.e. propositions which may be demonstrated to be true by reasoning. Geometry is also concerned with constructions, which are chiefly practical applications of the axioms and theorems.

Angles. In Fig. 1.1, *XO*, in making the complete rotation of 360° from *BO* to *BO*, passes through a series of angles to which specific descriptions are assigned (Table 1.4).

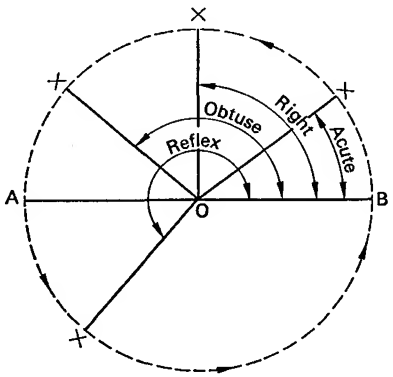


FIG. 1.1. Angles.

TABLE 1.4

Acute angle—less than 90°	Right angle—90°
Obtuse angle—between 90° and 180°	Reflex angle—between 180° and 360°
Complementary angles—sum to 90°	Supplementary angles—sum to 180°

Parallel straight lines are defined as straight lines in the same plane which, if produced indefinitely, cannot meet.

Transversals to parallel lines. A straight line which cuts two parallel lines makes the alternate angles equal, the corresponding

angles equal, and each pair of exterior angles and interior angles sum to 180°, i.e. two right angles. In Fig. 1.2:

Alternate angles: $A = D = W = Z$; $B = C = X = Y$.
Corresponding angles: $A = W = D = Z$; $C = Y = B = X$.
Exterior and interior angles: $A + B = C + D = W + X = Y + Z = 180°$.

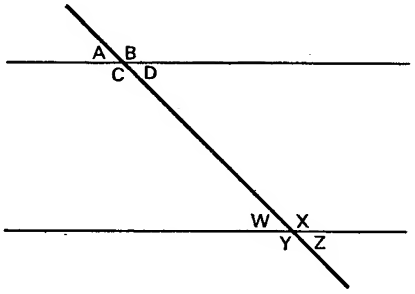


FIG. 1.2. Transversal to parallel.

The triangle is defined as a plane figure bounded by three straight lines. Triangles may be classified by the equalities or inequalities of their sides; where two or three sides are equal two or three angles are also equal:

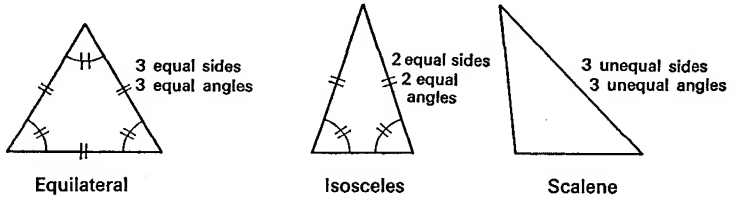


FIG. 1.3. Triangles classified by sides.

Triangles may also be classified by their angles:

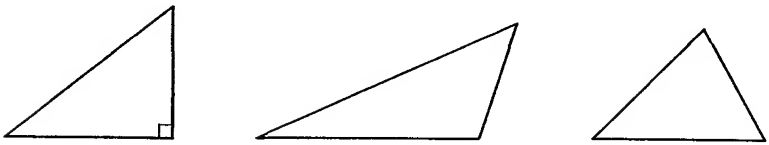


FIG. 1.4. Triangles classified by angles.

It should be observed that:

(a) A right-angled triangle may be isosceles or scalene.
(b) An obtuse-angled triangle may be isosceles or scalene.
(c) An acute-angled triangle may be equilateral, isosceles, or scalene.
(d) In any triangle the greatest side is opposite the greatest angle.
(e) Any triangle must have two acute angles.

Right-angled triangles. The side opposite the right-angle is the hypotenuse [by (d) above it is the greatest side]. The square on the hypotenuse, i.e. the length squared, is equal to the sum of the squares on the other two sides. This is the theorem of Pythagoras. If any two sides of a right-angled triangle are known the third can be calculated by Pythagoras' theorem:

(a) The sides which include the right angle are 4 units and 3 units; find the hypotenuse.
$4^2 + 3^2 = 16 + 9 = 25$. The square root of $25 = 5$. The hypotenuse is 5 units.
(b) The squares on the hypotenuse and one other side are 169 cm and 144 cm respectively. Find the remaining side.
$169 - 144 = 25$. The square root of 25 is 5. The side is 5 cm.

Congruent and similar triangles. Triangles are said to be congruent when they are equal in all respects; when the three sides of a triangle are equal to the three sides of another, the three angles

of each triangle must also be equal—i.e. congruence. If two triangles are equiangular but unequal in size, their corresponding sides are in proportion and the triangles are described as 'similar'.

The Angles of a Triangle Together Equal Two Right Angles.

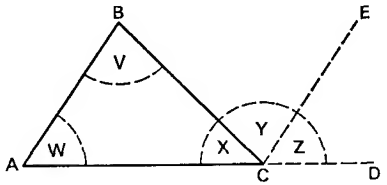


FIG. 1.5. The sum of the angles of any triangle.

See "Transversals" (p. 15). Draw CE parallel to AB. Produce AC to D. $Y = V$; $Z = W$; $X + Y + Z = 180°$.

Definitions (Fig. 1.6)

Circles. A point which moves on a plane at a fixed distance from a further fixed point describes an arc or circumference of a circle; this defines a circle.

Radius. A straight line from the centre to the circumference of a circle. All radii of a given circle are equal.

Chord. A straight line which joins two points on the circumference of a circle.

Diameter. A chord which passes through the centre of a circle.

Segment. The area enclosed by chord and arc.

Sector. The area enclosed by two radii and the arc they cut off.

Tangent. A straight line which touches a circle externally. A radius which meets the tangent at its point of contact with the circle is at right angles with the tangent.

Concentric circles. Circles having a common centre.

Ratio of circumference and diameter. 3·14159 . . . , usually shortened to 3·142 or, less critically, to 22/7; symbolized by π (the Greek letter pi). Therefore the length of the circumference is πD (where D is the diameter) but more often written as $2\pi r$ (where r is the radius).

Circular measure. The division of the circumference into 360 degrees has served and continues to serve very many purposes in pure and applied mathematics. However, the radian is more rational since it is an arc which is equal in length to a radius: thus there are 2π radians to the circumference. The radian is approximately 57·3 degrees.

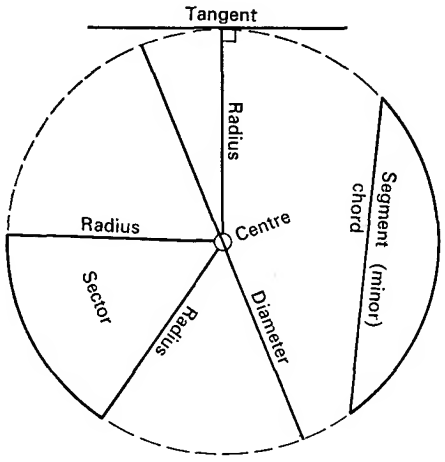


FIG. 1.6. Adjuncts of the circle.

TRIGONOMETRY

Introduction. Pure trigonometry is applied to the solution of triangles, i.e. given incomplete information on angles and sides it is possible to calculate the whole, including area. Surveying, navigation, and astronomy are among the most important of the many fields which find wide uses for this branch of mathematics.

Given a triangle ABC right-angled at C with lines drawn internally parallel to BC, it is evident that, since they are equiangular, the three triangles so formed are similar and that consequently their corresponding sides are proportionate (Fig. 1.7):

$$\text{(a)}\ \frac{BC}{AB} = \frac{B_1C_1}{AB_1} = \frac{B_2C_2}{AB_2}, \qquad \text{(b)}\ \frac{AC}{AB} = \frac{AC_1}{AB_1} = \frac{AC_2}{AB_2},$$

$$\text{(c)}\ \frac{BC}{AC} = \frac{B_1C_1}{AC_1} = \frac{B_2C_2}{AC_2}.$$

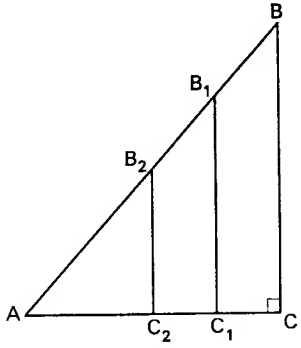


FIG. 1.7.

It is further evident that the ratios (a), (b) and (c) are separately associated in some manner with the angles of the triangle. It is convenient and customary to denote the angles by capitals and the opposite sides by the same small (lower case) letters; thus side a is opposite angle A, side b is opposite angle B and adjacent to angle A, while side c is opposite angle C and is the hypotenuse of the right-angled triangle.

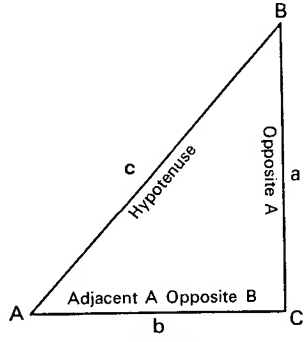


FIG. 1.8.

The basic trigonometrical ratios.

$\frac{a}{c}$ $\frac{\text{opposite}}{\text{hypotenuse}}$ is the sine of angle A.

$\frac{b}{c}$ $\frac{\text{adjacent}}{\text{hypotenuse}}$ is the cosine of angle A.

$\frac{a}{b}$ $\frac{\text{opposite}}{\text{adjacent}}$ is the tangent of angle A.

These ratios are usually abbreviated sin, cos, and tan, and the values for all angles may be obtained from mathematical tables.

Heights and distances. (a) Measured from a point on the horizontal ground 40 m from a vertical flagstaff the angle of elevation of the top of the flagstaff is 39°. Find the height of the latter.

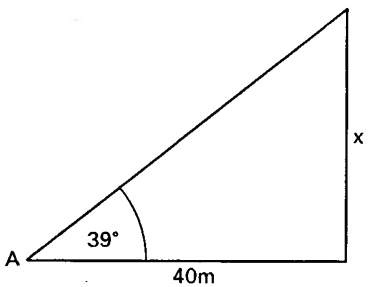


FIG. 1.9.

From Fig. 1.9 let x represent the flagstaff and A the point of observation. Then $x/40 = \tan A$ and $x = 40 \tan 39°$. From tables, $\tan 39°$ is $0{\cdot}8098$; therefore the height is $40 \times 0{\cdot}8098 = 32{\cdot}392$ m; say $32{\cdot}4$ m.

(b) A 20 ft ladder leaning against a vertical wall makes an angle of 60° with the pavement. Find the height of meeting the wall.

From Fig. 1.10, let x represent the height. $x/20 = \sin 60°$; $x = 20 \times 0{\cdot}8660$ (from tables) $= 17{\cdot}32$ ft.

(c) A rope is stretched taut from a tower to the ground 10 ft from the base of the tower. The length from tower to ground is 40 ft. Find the angle between rope and ground.

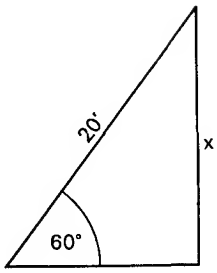


FIG. 1.10.

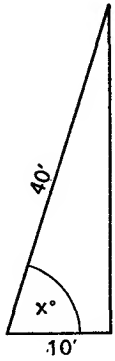


FIG. 1.11.

From Fig. 1.11 find x. $\cos x = 10/40 = 0{\cdot}25$, which (from tables) equals 75° 30′.

Most of the tables are provided with both natural ratios and log ratios. For more difficult work it is desirable to use the logs direct. Areas involving the ratios are considered under 'mensuration' below.

MENSURATION

Areas

Quadrilaterals. The quadrilateral is a figure bounded by four

straight lines; the rectangle, the parallelogram, and the trapezium are special cases of quadrilaterals.

The rectangle has four right angles and pairs of opposite parallel sides, i.e. it is a square or oblong. The area of the former is a side squared, that of the latter is length × breadth.

The *parallelogram* has parallel opposite sides and equal opposite angles; a rhombus is a parallelogram with all its sides equal; the area is base × height, the latter being the perpendicular distance between parallel sides. Since a diagonal divides a parallelogram into two congruent triangles, the area is twice that of a triangle on the same base.

The triangle has an area of half its height × the base; the height is defined as the perpendicular distance from a vertex to the opposite side which then becomes the base. Where the length of all the sides is known the area may be calculated from the formula

$$\sqrt{[s(s-a)\,(s-b)\,(s-c)]}$$

where s is $\frac{1}{2}(a+b+c)$. If two sides and the included angle are known, the following trigonometrical formulae may be applied:

$$\tfrac{1}{2}\,bc \sin A \quad \text{or} \quad \tfrac{1}{2}\,ac \sin B \quad \text{or} \quad \tfrac{1}{2}\,ab \sin C.$$

The area of a circle is determined by the formula πr^2, where r is the radius.

The total surface of a rectangular solid—such a figure has six faces; in a cube they are all equal and therefore the area is side^2 × 6. Other rectangular solids have three pairs of equal faces and the total area is: face a (length × breadth) × 2 + face b (length × breadth) × 2 + face c (length × breadth) × 2.

The total surface of a cylinder is the sum of the areas of the circular top and bottom with the area of the curved surface: $2\pi r^2 + 2\pi rh$, where r is the radius and h the height.

The curved surface of a cone is πrl, where l is the length of the slant side.

Volumes

Rectangular solid. If the solid is a cube, the volume is side^3, otherwise the volume is length × breadth × height.

Cylinder. $\pi r^2 h$ (for a right circular type).

Sphere. $\frac{4}{3} \pi r^3$.

Cone. $\frac{1}{3} \pi r^2 h$, where h is the vertical height.

The slide rule. This is an instrument which reduces many mathematical operations to observations of a scale or scales. It consists of a slide which moves in the centre of several fixed scales each serving a different purpose.

(In the figure it should be noted that the subdivisions have been omitted for clarity.)

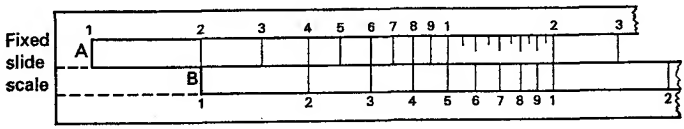


FIG. 1.12. A simplified portion of a slide rule.

A simple example of multiplication and division is demonstrated in Fig. 1.12. For the former process the digit 1 on the sliding scale B is registered with the first factor on the fixed scale A and the result is shown at the point on scale A where the second factor on scale B meets it. Thus $2 \times 2 = 4$; $2 \times 3 = 6$; $2 \times 4 = 8$; and so on. For division the operation is reversed; using the same relation of the scales the dividend on scale A is connected with the divisor on scale B and the quotient appears where 1 on the slide coincides with the number on scale A.

The scales are graduated in the proportions of the logarithms of the ordinary numbers and therefore the slide rule carries out automatically the processes of addition and subtraction of the logs and the conversion to numerals; a further consequence is that the decimal point must be inserted where necessary by inspection.

The normal forms of the slide rule carry three fixed scales with three others on the slide connected by a hair-line cursor and, as well as the operations given above, they are designed for the calculation of square and cube roots, squares and cubes, and areas of circles with variations according to purpose and price.

CHAPTER 2

Measurement

Introduction. It has been said that "science is measurement" and while this is, perhaps, too simple to be wholly true, there is no doubt of the importance of measurement in science, industry, and everyday life.

In the public interest all states have established standards of weights and measures and probably all of them have adopted some method of inspection to ensure that purchasers get the specified quantities and that the measuring instruments are not "adjusted" in the vendor's favour.

In the United Kingdom, some Commonwealth countries, and the United States, the measures in ordinary use have been handed down from a distant past and many refer to familiar objects; thus an inch (the word is the Latin *uncia*—a twelfth) is supposed to be the size of the thumbnail; the foot means what it says (clearly they were giants in those days); and the mile (Latin *milia*—thousands) from a thousand strides of the Roman soldier; the biblical cubit is the length of the forearm. There are special units for special purposes: the furlong on the racecourse; the hand for the height of horses; the fathom for sea-depths and the nautical mile; there are the familiar ens, ems, and points of the compositor. Rods, poles, and perches—the measures of capacity or volume, and the pharmacist's grains and scruples (now becoming obsolete) are even more complex.

While these many measures must not be assumed to be wholly irrational, few would contest the need for simpler standards with, if possible, a common basis.

THE METRIC SYSTEM

The French Revolution did more than shake or shatter the world's traditional political patterns. In 1791 a committee of the Academie Française recommended the adoption of a single uniform system of weights and measures all of which were derived from the measure of length. The French Assembly did not act with the celerity it displayed in other matters, but the metric system was eventually accepted and it spread rapidly through the many parts of Europe under French influence as a consequence of the conquests of the Revolutionary Army and the later Napoleonic Imperialism. The system is in use today for general purposes all over the world other than in Great Britain, parts of the Commonwealth, and in the United States, and its adoption in these territories is probably inevitable since its use is permissive already, and every laboratory and scientific institution here and everywhere else has accepted it.

The metre. The basis of the system is the metre which was originally calculated as the ten-millionth of the earth's quadrant from the Equator to the North Pole; however, this was later found to be in slight error, and for most purposes the standard is the International Prototype Metre. This is the distance at 0°C between two lines in the platinum–iridium rod deposited in the vaults of the International Bureau of Weights and Measures at Sèvres, near Paris, France. The most refined, or perhaps cosmic, definition sets down that the metre is 1 650 763·73 times the wavelength of the orange radiation of the isotope A.W 86 of the rare gas krypton.

The gram. This was originally intended to be equal to the mass of one cubic centimetre (1 cc) of pure water at its densest at 4°C; this is no longer held to be satisfactory and the gram (or gramme) is defined as one-thousandth of the International Prototype Kilogram which is preserved at the International Bureau as above.

The litre. This is the standard measure of capacity and it is also referred to the prototype at Sèvres; this is a cube of one decimetre side (see below for the prefixes).

Multiples and subdivisions. The authors of the metric system adapted the Greek numerals for multiples of the standard units and Latin equivalents for the subdivisions and, since the system is decimal, i.e. it proceeds by multiples or divisors of 10; few of these are needed in practice:

Multiples

Prefix	Mega	Kilo	Hecto	Deca
Factor	1,000,000	1,000	100	10

Divisors

Prefix	Deci	Centi	Milli	Micro
Divisor	10	100	1,000	1,000,000

The term 'micrometre'—one-millionth of a metre—has been almost completely replaced by 'micron' which is used, or subdivisions of which are used, for very small measurements such as the wavelength of light.

Of these prefixes, only kilo-, centi-, and milli- are likely to be encountered in ordinary usage.

While the metric units ought to be accepted as they are without reference to those they have displaced or are displacing, a few approximate equivalents appear below:

Kilometre (km)	Metre (m)	Kilogram (kg)	Gram (g)	Litre (l.)
0·621 mile	39·37 in.	2·2 lb	0·035 oz	1·76 pint

Time. The units used to express the passage of time are unique in that they have been carried over from the classic world without

fundamental alteration other than those made necessary by the increasing refinement of observation since they are derived, in principle, from natural events.

The year is defined generally as the time taken by the earth to complete its path, or orbit, round the sun; this period is approximately 365·24 days and, since the normal year is 365 days it is necessary to make adjustments for the fraction by the addition of an extra day every fourth or leap year with further adjustments at long intervals.

The day is the time taken for the sun to make its apparent circuit of the earth; very slight variations occur and these are corrected by the adoption of a mean or average solar day.

The mean solar day is divided into 24 hr each of 60 min; a minute is further divided into 60 sec. It should be noted that the day and its subdivisions are expressed in a form of the duodecimal scale of notation (see the section on arithmetic, p. 4).

The week and the month may be considered to be rather arbitrary divisions of little importance in the present context.

MEASURING INSTRUMENTS

Distance or length. The simplest device to measure distance is the rope or stick, knotted or notched as required, but obviously with little adaptability or accuracy. The rule, of which the length (metre, yard, or foot) is divided into centimetres and millimetres or into inches and fractions, is not limited in the same manner.

Long distances may be calculated with great accuracy by means of optical instruments which apply the principles of trigonometry and binocular vision; the range-finder is the most familiar of these instruments. The determination of distance depends upon the solution of a triangle given that the length of one side, usually the base, and two angles are known (Fig. 2.1).

$$c/a = \tan C, \text{ i.e. } c = a \tan C.$$

In Fig. 2.1 the calculation is simplified since a right angle is shown; in any case, most of the instruments record the desired distance more or less automatically.

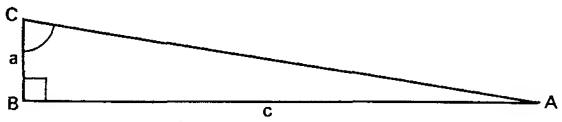


FIG. 2.1.

For the measurement of small distances, as for machine parts where great precision is necessary, various instruments are available which range from the deceptively simple to the obviously complex; the best known among these are the vernier and the micrometer.

The vernier. The vernier slide gauge may be considered a development of the simple rule in which the main scale is marked in centimetres or inches and subdivided in the usual manner into millimetres or tenths of an inch respectively, and a sliding or movable scale in which nine-tenths of the unit of the main scale is divided into ten equal parts, the lines of each of the scales being in contact (Fig. 2.2).

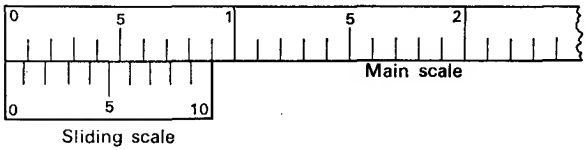


FIG. 2.2. The vernier gauge.

Therefore the difference between one subdivision of the main scale and one division of the sliding scale (or vernier) is 0·01 cm (or 0·1 mm) or 1/100th in. according to the units used.

In the use of the instrument the distance to be measured is that between the zero of the main scale and the zero of the sliding scale. The whole number of units is that which appears to the left of the sliding scale zero: the first decimal place is read from the subdivision of the main scale immediately to the left of this zero; the second decimal place is shown at the point on the vernier

where a main scale subdivision and vernier division coincide. In the example (Fig. 2.3) the distance is fractional; the first decimal is 6 and the second place at the coincidence of the scales is 7. Thus the distance under examination is 0·67 cm (while metric units are considered, inches may, of course, be substituted).

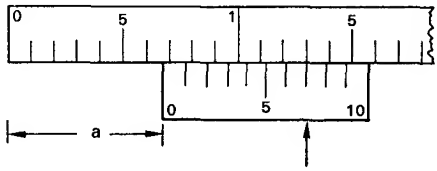


FIG. 2.3.

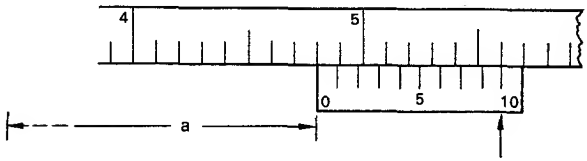


FIG. 2.4.

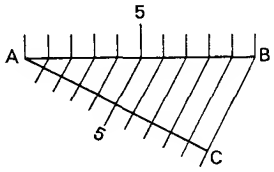


FIG. 2.5.

In Fig. 2.4 the measurement recorded is 4·79 cm.

The production of the vernier gauge and to some degree the principle governing its operation are applications of a geometrical theorem on parallels (Fig. 2.5).

In the triangle *ABC*, if the side *AB* is divided into ten equal parts

and parallel lines are drawn from each part to meet AC, the latter is also divided into ten equal parts.

Therefore if the side AC = nine-tenths of AB, each tenth part of AC = nine-tenths of each part of AB.

The vernier gauge in its simplest form is considered above. However, while complex instruments capable of greater refinement are available, they do not depart from the principles shown. Among the more familiar forms are the vernier callipers in which the main scale is attached to a fixed point or head with a similar point on the slide. This instrument is particularly adapted to the measurement of the external dimensions or internal diameters of tubes or other curved shapes.

The micrometer. This instrument is considered capable of greater accuracy in the measurement of small distances than the vernier callipers. It depends essentially on the rotation of a screw through

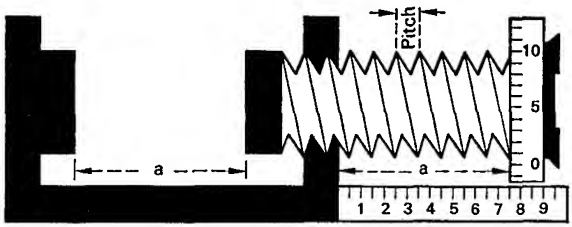


FIG. 2.6. Principle of the micrometer.

a nut, each revolution moving the stem of the screw through a distance equal to the screw's pitch; the latter is defined as the space between adjacent crests of the thread of the screw.

The lengthwise movement of the screw is indicated on a scale; the head of the screw, which controls the rotation, is marked around its circular edge or face in equally spaced divisions in such a manner that, if the division is one-fiftieth of the circumference, a movement of the head by one division moves the screw in the direction of its length by one-fiftieth part of the pitch (Fig. 2.6).

In the most familiar form of the instrument, the object to be measured is placed between the fixed point attached to the main

scale and the movable point attached to the screw—this distance corresponds to the distance *a* of Fig. 2.6; the main scale is engraved on the sleeve and the rotating scale on the thimble.

As may be expected, the two systems of measurement current in the United Kingdom, the United States, and elsewhere are in use on micrometers. As most usually encountered these are applied as:

(i) Fractions of an inch on the sleeve scale with a pitch of 1/40 in. (0·025 in.) with 25 divisions on the thimble. Each division on the latter therefore indicates 1/1000 in. (1/40 × 1/25), i.e. 0·001 in. In Fig. 2.7a, 2¼ appears on the sleeve indicating 0·225 in., with 16 on the thimble, which stands for 16/1000ths in., that is 0·016 in. thus the distance is 0·241 in.

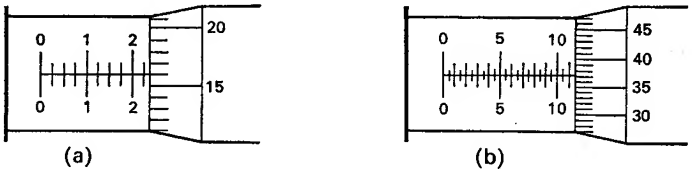


FIG. 2.7.

(ii) In metric micrometers the sleeve is engraved in millimetres and, since the pitch is 0·5 mm, two rotations of the thimble are necessary for a movement of 1 mm; the thimble has fifty divisions and thus each represents 0·01 mm. In Fig. 2.7b 11 mm of the sleeve scale are added to the 0·37 shown on the thimble to give a distance of 11·37 mm (often expressed as 1·137 cm). It should be noted that the sub-subdivision of the millimetre does not appear on the sleeve and that therefore the first rotation of the thimble is assumed.

Volume or capacity. The popular measures of volume are almost obsolete for scientific and technological purposes in those countries in which the metric system is otherwise only accepted in part; thus laboratory-measuring glassware is everywhere defined in litres and millilitres.

The graduated measuring cylinder. This vessel affords the most

rapid—if not the most accurate—means for the measurement of volume. It ranges in capacity from as much as 2 l. to as little as 10 ml or even less. All are subdivided by engraved or etched lines.

The pipette. The pipette is a glass tube enlarged to a bulb towards its centre for other than the smallest sizes. It is calibrated to deliver its stated volume the measure of which is indicated by a line in the upper part. The instrument is operated by mouth suction in normal practice, but mechanical appliances are available and very much desirable for use with poisons; it is filled above the mark and the liquid allowed to escape slowly to fall to that mark. All the normal liquids—the majority being aqueous solutions—form a curve or meniscus with the edges in contact with the container turned upwards; measurements must be made with the lower part of the meniscus on the indicator line and observations must be carried out at eye-level.

The burette. This instrument may be considered a development of the pipette, but it is intended to deliver a definite but variable volume of liquid under the control of a tap below. Burettes are made in many capacities, but it is probable that that of 50 ml capacity is the most familiar. The remarks above on the importance of the meniscus and eye-level observation apply with equal force.

Weight. Metric measurements, again, have all but superseded the traditional in the present context; the gram is supreme.

The chemical balance in its simplest form consists of two pans each suspended to one arm of the beam. The latter is supported at its centre on a knifelike agate edge (agate is a very hard natural compound, chiefly silica and rather resembling flint). These balances are usually provided with a plumbline to effect accurate vertical and horizontal adjustment of the instrument, and a pointer —which swings over a scale at is lower end—is attached to the beam.

Weighing is carried out by adding the material to the left-hand pan and the weights to the right-hand pan—in both cases only with the pans at rest. The normal weights range from 100 g downwards to the fractions; they are provided in such units that any weight is possible from the maximum to the smallest of the fractions.

Students will have quickly appreciated that the balance is designed to weigh the given material and not to weigh to a given amount—a rather subtle but vital difference.

Equivalence is determined by equal movements of the pointer to the left and right of the central point of its scale but never when it is at a standstill.

This simple balance has been developed to provide self-recording apparatus for work at the highest levels (and at a price in that category) capable of weighing to 10^{-7} g, i.e. to 1/10,000,000 of a gram.

Telling the time. The passing of time was once recorded by such methods as the burning of marked candles in which each division represented, it was hoped, some period of time, and by hour-glasses—still familiar as egg-timers (in minutes)—in which sand trickles from the upper glass compartment to the lower. Spring-motivated watches and similar or weight-operated clocks are the most familiar means today for the measurement of time although the latter tend to be replaced by battery or mains electric instruments.

Latitude is fairly easily ascertained by observation of the stars, and particularly by means of the sextant; indeed, early navigation meant little other than reaching the required latitude and sailing east or west to the landfall or port. The determination of longitude demands an accurate timekeeper since it is calculated from the difference between local and Greenwich time. In 1714 an Act of Parliament authorized a reward of up to £20,000 for a means of estimating longitude with reasonable precision. John Harrison (1693–1776) received the highest award, with some difficulty, for his chronometer of 1735 in 1765. In this instrument Harrison solved the problems due to the differential heat expansion of the various metals used in clockmaking and that of devising an accurate escapement to control the tension of the spring. Although radiotelegraphy has become of great importance, the chronometer remains a valuable instrument of navigation.

Temperature. This subject and the means for its determination are considered in Chapter 5.

Metrication and SI. SI is the abbreviation of *Système International d'Unités* and it is an extension and refinement of the metric

system. There are six basic units: these are all explicable in terms of the normal system, but some of them are larger and some more precisely defined or named.

Thirty countries have already approved SI, and in the United Kingdom many academic institutions and examining bodies are taking steps, encouraged by the Royal Society, to adopt the system.

The Joint Committee for National Certificates and Diplomas in Printing is among the bodies to decide that S.I. metrication should be adopted.

However, it need not be supposed that all the metric units given in this book and elsewhere have suddenly become obsolete; they will continue in use side by side with SI (Table 2.1) as the latter is accepted.

TABLE 2.1. THE BASIC SI UNITS

Physical quantity	Name of unit	Symbol for unit
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	degree Kelvin	°K
Luminous intensity	candela	cd

All other units are derived from and are expressed in terms of the above.

The specification of paper substance in metric units had already been supported, but the displacement of the gram by the kilogram as the S.I. unit of mass involves, for this purpose, the substitution of kg/m^2 for g/m^2 (or $kg\ m^{-2}$ for $g\ m^{-2}$).

Parallax. The probability of error due to a change in an observer's position is discussed in the chapter on light and optics. Here it is stressed that all recording or measuring apparatus must be viewed from directly in front so that pointer or engraved line are vertically above the scale or object being measured.

Part II

Physics

CHAPTER 3

Physics: Mass and Density

Introduction to physics. Physics may be said to be that branch of science concerned with energy and the properties of matter, but it cannot be too often emphasized that the sciences do not exist in isolation although the contacts between them appear, perhaps rather paradoxically, mostly at the higher levels.

Physics is most closely related to chemistry. It has, indeed, been said that the latter becomes more and more explicable in terms of physics while physical chemistry itself deals with so many subjects which may be reasonably referred to physics and, of course, the converse.

That part of chemistry which is devoted to the structure of matter might equally well have been placed in this part of the present work, but it is conventional and, indeed, convenient to deal with it in the manner adopted.

Therefore for the purposes of this book it is possible to consider many physical topics on their own merits without necessarily referring them to that basis shared by both physics and chemistry.

The standard introductory question to this subject is "Which is the heavier—a pound of lead or a pound of cotton-wool (or cork or feathers)?" Obviously neither is heavier, but equally obviously a given volume of lead weighs much more than the same volume of cotton-wool. It may be objected with good reason that the fibres of cotton-wool enclose a lot of air, and the comparison is more effective if the pair of examples are lead and aluminium; in fact, given equal volumes, lead is about $4\frac{1}{3}$ times heavier than aluminium.

The phenomenon of weight is due to the attraction, or force of gravitation, between the vast substance of the earth and that of a smaller body; the attraction is mutual, but that of the former is overwhelmingly evident. The moon is very much smaller than the earth and, therefore, again given the same volume, lead would appear to be only about one-sixth of its earthly weight on the satellite provided that a spring balance is used; if a counterweight balance is employed there would be no difference since the attraction is exerted in both cases on sample and weights. If it became possible to conduct the experiment on the surface of a giant star, no spring balance could support the lead since the attraction would be enormous.

It is, nevertheless, apparent that whether the metal is on earth, moon, or star, its substance, i.e. its mass, is unaltered, and it is consequently necessary to establish some means of stating mass in terms strictly independent of weight although mass and weight may appear for many purposes to be identical.

Density and specific gravity. Density is defined as the mass of a unit volume of a substance; otherwise stated this is:

$$\text{Density} = \frac{\text{Mass of material under examination}}{\text{Volume of the material}}.$$

It is obvious, however, that density in these terms must have a reference to the units employed, and, for example, the statement that a substance has a density of 150 lb/ft^3 is properly an expression of absolute density which is of little value for comparison unless the same units are in general use.

Specific gravity or relative density is a pure number and a precise standard of reference. It is defined as the relation between the density of a substance in given conditions and the density of an equal volume of water in the same conditions. Stated more briefly this is:

$$\text{Specific gravity} = \frac{\text{Mass of material under examination}}{\text{Mass of equal volume of water}}.$$

Since the mass of 1 cc of water at 4°C is 1 g, where density is expressed as the relation of the mass of 1 cc of a material to that of 1 cc of water, density and specific gravity are numerically the same.

Specific gravity of a solid. If the solid under examination is rectangular or of other geometrical form of which the volume may be easily calculated, SG is assessed when the weight of the solid is obtained; two examples are given.

Calculate the SG of two solids given the information:

(a) A cube of 2·65 cm side; weight 94·55 g.
(b) A sphere of 8·72 cm diameter; weight 3246 g.

(a) The SG is $\frac{\text{(mass) } 94{\cdot}55}{\text{(volume) } 2{\cdot}65^3}$.

No.	Log
94·55	1·9756
$2{\cdot}65^3$	0·4232
	×3
	1·2696
	1·9756
	1·2696
	0·7060

$= 5{\cdot}082.$

(b) The SG is $\frac{\text{(mass) } 3246}{\text{(vol. sphere) } \frac{4}{3}\pi r^3}$

$(r = \frac{\text{diameter}}{2})$.

	No.	Log
	3246	3·5113
$\frac{4}{3}$	1·333	0·1249
π		0·4972
	$4{\cdot}36^3$	0·6395
		×3
		1·9185
		2·5406
		3·5113
		2·5406
		0·9707

$= 9{\cdot}348.$

When the substance is an irregular solid for which it would be difficult or impossible to determine the volume, the principle of Archimedes may be applied. The classic story of the philosopher, the supposed adulterated royal crown, and the triumphant *eureka* is too well known to need repetition. The principle is based upon the phenomenon that when an object is immersed in a liquid it has an apparent weight loss equal to the weight of the liquid it displaces.

The experimental determination of SG may be undertaken with little difficulty if without great accuracy by the use of a displacement or *eureka* can in which a corollary of the principle is applied, i.e. that the volume of the displaced liquid is equal to that of the solid. The can is a metal vessel with a downward spout. Filled with water to the junction of spout and vessel, the immersion of the solid in the water displaces some of the liquid which overflows to be collected in a small graduated cylinder.

For example, given that the dry weight of the solid is 150 g and that the water displaced has a volume of 25 cc, which is equivalent to a weight of 25 g, the SG of the solid is $\frac{150}{25}$ or 6.

It is possible with lower accuracy merely to immerse the solid in water contained in a graduated cylinder and to observe the rise in the water level.

The principle is better applied, certainly with more precision, by weighing the solid in air in the normal manner and weighing it suspended from the beam of a chemical balance into a beaker of water supported over but out of contact with the pan; alternatively, a good spring balance may be used for both weighings. The method of calculation may be stated as a formula:

$$\text{SG} = \frac{\text{Weight of the solid in air}}{\text{Weight of solid in air—weight of solid in water}}$$

(the denominator may also be stated as "weight loss of solid in water").

For example, given that the weights in air and water of the solid are respectively 254·6 g and 223·3 g, the weight loss is 254·6 – 223·3 g, i.e. 31·3 g. The calculation is:

$$\frac{254 \cdot 6}{31 \cdot 3}$$

No.	Log
254·6	2·4058
31·3	1·4955
	0·9103

$$= 8 \cdot 134$$

Estimation of "voids" in printing metals. Knowledge of the SG or density, however expressed, of the materials, and particularly the metals of engineering and construction, is very important indeed. This applies to the design and manufacture of the presses and other apparatus of the printing industry; of considerable interest in the present context is the estimation of the air bubbles or voids which may occur in any casting of molten metals and particularly in those printing metals for slugs, type, and stereos which are subject to rapid cooling.

This matter is discussed briefly in Chapter 15, on printing metals; here it is proposed to apply the principle of Archimedes and to give an example of the calculation.

The SG of the metal should be known; otherwise it may be found experimentally as shown above. It is apparent that if the metal as cast contains voids, the same experimental practice will show a lower SG according to the extent of the porosity.

Therefore being given or having ascertained that the SG of a perfect sample of the metal under examination is 9·74, that of suspected cast is found to be 9·46. Since the proportion of voids is normally expressed as a percentage, the formula is:

$$\left(1 - \frac{\text{SG (or density in g/cc) of suspected cast}}{\text{SG (or density in g/cc) of perfect metal}}\right) \times 100;$$

this, applied to the present calculation, is

$$\left(1 - \frac{9 \cdot 46}{9 \cdot 74}\right) \times 100.$$

$$1 - 0{\cdot}9317 = 0{\cdot}0683$$

$$0{\cdot}0683 \times 100$$

$$= 6{\cdot}83 \text{ per cent.}$$

No.	Log
9·46	0·9579
9·74	0·9886
	$\bar{1}$·9693

This is an example of a relatively low or even a normal proportion of voids; amounts of more than double this are not uncommon.

Flotation. The totally immersed body is subject to an upward force or thrust from the liquid, and it is to this force that the apparent loss of weight is due.

A body floats when its SG is lower than that of the liquid and this applies equally to the piece of cork and the battleship, but while the former may be considered as homogeneous, the density of the ship is an average of that of each of its many components.

A floating body moves downwards into a liquid to the point at which a volume of liquid having a weight equal to that of the body is displaced and an equilibrium is established; thus a body of low density—such as cork—rides almost on the surface of the water, while ice with a density of about 0·9 g/cc just floats with almost nine-tenths of its volume submerged.

It is clear from the above that as cargo is taken into a ship its average density increases and the lower it sinks into the water. Samuel Plimsoll's long campaign to prevent dangerous overloading culminated in the Act of Parliament of 1876 which enforced the marking of lines on the hulls of ships to indicate the maximum loading levels. Since the density of water varies with temperature and salt content, lines at different levels indicate maximum loading in temperate and tropical summers and winters and in the fresh waters of the great rivers.

SG of liquids. A standard method for the determination of the SG of a liquid involves the use of a density or SG bottle; this vessel is a small flask with a ground-in glass stopper pierced with a fine hole. In use the bottle and stopper are accurately weighed; the bottle is then filled with distilled water and the stopper re-

placed, any excess liquid is forced through the perforation to be carefully wiped away. Liquid and vessel are reweighed and the latter is emptied as completely as possible. The bottle is given a swill with a little of the test liquid to remove any remaining water, the vessel is charged with the test liquid, and the whole weighed.

Given that the information obtained is the following:

(a) Weight of bottle and stopper, 15·45 g;
(b) Weight of bottle, stopper, and water, 22·64 g;
(c) Weight of bottle, stopper, and test liquid, 21·95 g;

the calculation is:

(i) Weight of water is $22{\cdot}64 - 15{\cdot}45 = 7{\cdot}19$ g;
(ii) Weight of test liquid is $21{\cdot}95 - 15{\cdot}45 = 6{\cdot}50$ g;
(iii) SG of test liquid is $\frac{6{\cdot}50}{7{\cdot}19}$.

No.	Log
6·50	0·8129
7·19	0·8567
	$\bar{1}$·9562

$= 0{\cdot}904.$

In practice, various forms of hydrometer are widely used. These instruments are usually of glass, but brass is favoured for some industrial purposes, with an elongated bulb at the lower end weighted with mercury or small lead shot and with the scale in the tubular stem above the bulb. The accuracy of the hydrometer rests upon the calibration of the scale and the care of the observer.

It will be apparent from the matter above on flotation that the lower the SG of a liquid the lower the instrument will sink and the converse.

Hydrometers are available in sets to cover between them a wide range of SG readings. There are also special purpose instruments to measure the density of milk—the richer the milk the higher the SG; the alcohol content of fermented liquors, since the greater the alcohol component the lower the SG; and also hydrometers with more or less arbitrary scales. Among the latter is the Baumé

hydrometer used to assess the ferric chloride concentration of the mordant for copper in photoengraving and photogravure and which is frequently employed to test the density of the various light-sensitive coating solutions of the first-named process and in photolithography.

A further hydrometer of printing interest is the argentometer used in the wet collodion process to record the rather critical concentration of the silver nitrate bath. It is supposed, somewhat dubiously, to state concentration in grains to the fluid ounce; the doubt arises because, during use, other salts are formed which contribute to the overall density of the bath.

Density of gases. The density of a gas may be obtained by the use of a large, stoppered vessel of known weight and capacity. A gas heavier than air, such as carbon dioxide, is led into the vessel by a tube which reaches the bottom, the opening of the vessel being uppermost. The action is continued until it is assumed that all the original air has been displaced by the heavier gas. When the test gas is lighter than air, as, for example, hydrogen, the vessel is inverted and the air expelled by downward displacement.

The experiment is more easily undertaken if the vessel is provided with a tap and is air-exhausted by a pump. The test gas is then passed into the vessel, the tap closed, and the whole weighed.

Given that the vessel is of 2 litres capacity, that the weight of the vessel is 248·1 g, and that the weight of the vessel and test gas is 248·28 g, the calculation is:

Weight of the test gas is $248 \cdot 28 - 248 \cdot 1 = 0 \cdot 18$ g.

Density in g/cc of the test gas is $\frac{0 \cdot 18}{2000}$

$= \frac{0 \cdot 00018}{2} = 0 \cdot 00009$, or by logs

No.	Log
0·18	$\bar{1} \cdot 2553$
2000	$3 \cdot 3010$
	$\bar{5} \cdot 9543$

$= (0 \cdot 00009001)$ 0·00009.

This is the density in g/cc of hydrogen, but it is necessary to note that the volume of a gas is influenced by temperature and pressure

(see the gas laws in Chapter 5) which have small importance in the cases of solids and liquids. In the worked example it is assumed that the volume of the gas in the room temperature of the experiment has been adjusted to 0°C and the pressure to 273 mmHg, i.e. to standard temperature and pressure (STP).

Density of printing inks. Printing inks are by definition liquids, some being obviously so, but many letterpress and lithographic inks have such a high viscosity at rest that assessment of their density by the methods given above for liquids is likely to be ineffective. For some purposes an estimation of density is obtainable with some difficulty by filling a shallow receptacle of known weight and volume with the ink under test and weighing the whole. It is essential that the surface of the ink is exactly levelled to the containing vessel.

An alternative to the above is a small sheet of heavy glass with a recess to receive the ink. It is difficult to ensure precision in the volume of the recess, but the levelling of the ink's surface is assisted by the surrounding glass.

The weight of the ink is obtained by subtracting that of the vessel or glass former from the gross weight of ink and carrier; the density in g/cc is calculated by

$$\frac{\text{Weight of ink (g)}}{\text{Volume of container (cc)}},$$

and, given this information, the ink may be specified in the manner usually required, i.e. as the volume of a given weight. For example, having shown experimentally that 25 cc of the ink has a weight of 35 g, then 100 g will occupy $\frac{25}{35} \times 100$, i.e. 71·43 cc.

CHAPTER 4

Force, Energy, Mechanics

Introduction. Any consideration of the subjects which head this chapter must almost inevitably start with, or bring in at some stage, the great Newton's primary laws of motion; these are:

(a) A body remains at rest or in uniform motion in a straight line unless action by an external force changes these states.
(b) The force is equal to the product of the mass of the body and the acceleration; the acceleration proceeds in the direction of the force.
(c) Every action is accompanied by an equal and opposite reaction.

It should be apparent that all machines, whatever their complexity and purpose, provide evidence of the validity of these laws.

Force

Force may be said to be, in its widest sense, any cause of physical action but it is more specifically defined as an agent external to a body which moves that body from a condition of rest, or which accelerates or decelerates it, or which changes its direction of movement.

Units of force. In accordance with Newton's second law, any unit of force may be expressed by the formula

$$F = ma,$$

where F is the force, m the mass of the body, and a the acceleration produced in the body. This is, after all, not particularly profound

since it is common experience that the heavier the body and the greater the velocity to be produced in it, the larger the magnitude of the force needed to effect these changes.

It is proposed to set down what are regarded as the basic units of force:

The dyne. This is accepted as the absolute unit of force. It is that force which, acting on a mass of one gram, produces an acceleration of one centimetre per second per second.

The poundal. This is that force which, acting on a mass of one pound, produces an acceleration of one foot per second per second.

However, it is necessary to observe that, in accordance with proposals for the adoption for scientific and technical purposes of some revisions of the basic metric units, it is likely that the unit of force will be the 'newton' symbolized by N and defined as kg m s^{-2}, where kg is the kilogram (another name may be given) m is a metre, and s a second (this is further considered in Chapter 2).

Forces combined. If two forces are employed in the same direction the resultant may be obtained by simple addition while, if they are directly opposed, the resultant may be shown by subtraction.

However, when two forces are applied at an angle they present the problem of partial opposition. If, for example (Fig. 4.1), forces

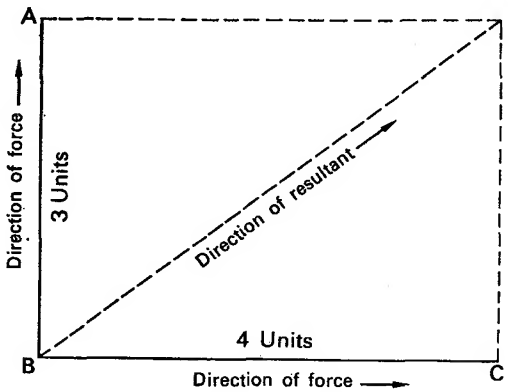


FIG. 4.1. Resultant of forces at right angles.

of 3 units and 4 units are exerted at right angles, the resultant is the diagonal of the rectangle whose sides are 3 and 4 units respectively. The solution may be found by careful construction but much more easily and accurately by the use of the theorem of Pythagoras.

The diagonal of the right-angled triangle ABC is

$$\sqrt{(3^2 + 4^2)} = \sqrt{25} = 5.$$

Therefore the resultant is 5 units.

Where, however, the two forces are exerted at other than right-angles, the resultant may also be found by construction and also, again with greater accuracy, by calculation.

For example, given that two forces of 2 units and 3 units respectively are disposed at an angle of 60° find the resultant (Fig. 4.2).

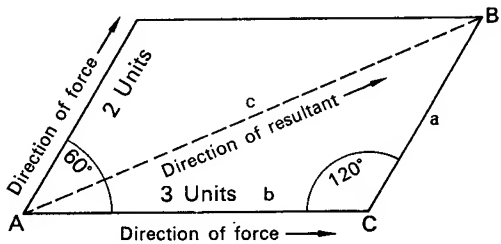


FIG. 4.2. Resultant of forces at an acute angle.

By construction the solution is about $4\frac{3}{8}$ or 4·37 units. In the calculation the matter is given—without proof—to indicate the mathematical method.

In a parallelogram the opposite sides and opposite angles are equal and the four angles together total four right angles or 360°. Thus, since the angle at A is 60°, the angle at C is 120° [360 − (60 + 60)] ÷ 2). In the triangle ABC, since two sides and the included angle are known, the cosine formula is applicable, i.e. $c^2 = a^2 + b^2 - 2ab \cos C$. (The sides are represented by lower case letters opposite the angles shown by capitals.) Further, since the angle C is obtuse, the cosine is that of (180 − 120)°, i.e. 60° with the negative sign.

Therefore, substituting in the formula:

(a) $c^2 = 2^2 + 3^2 - 2 \times 2 \times 3(-0{\cdot}5)$.

(b) $c^2 = 19$, and therefore $c = \sqrt{19}$, i.e. 4·359 units.

Vector quantities. Any quantity in which it is necessary to state direction as well as magnitude, as in the matter above, is a vector quantity. Other examples are velocity and acceleration. Vectors of any type may be combined by applying the parallelogram principle as in the instances above, and any number may be combined by selecting pairs and establishing the resultants; the final resultant is found by elimination, pair by pair.

Scalar quantities. When a quantity is adequately defined by magnitude only, as temperature, speed and time, it is described as scalar. Scalars may usually be combined by simple addition.

Energy

Energy may be briefly defined as the capacity of a body for doing work. The present standard unit for scientific and technological purposes is the erg, which is the work done by a force of 1 dyne moving through 1 cm. However, here again the unit which will ultimately be accepted (see under 'Metrication and SI' in Chapter 2) is the joule, symbolized by J and defined as kg m^2 s^{-2} in which the letters have the same meaning as for the newton above; the joule may be otherwise stated as equivalent to 10^7 (10 million) ergs.

For many purposes the foot-pound is still employed; this is the work done by the force of 1 lb acting over 1 ft.

Physical energy is usually understood to exist in two forms—potential and kinetic.

The former is defined as that which a body has by reason of its position or state; examples are the head of water held by a dam, a spring under tension, and a gas compressed in a cylinder. Chemically, potential energy is present in an explosive, in coal, and in the storage battery.

Kinetic energy is possessed by bodies in motion as in the moving car, the revolving flywheel, and the projectile travelling towards its target.

In assessing the total energy of an operation it is of no consequence whether the action is conducted in steps or as a single

whole. For example, if 100 bricks, each of 5 lb weight, are raised 40 ft in four stages of 10 ft, ten at a time, the total energy is $5 \times 4 \times 10 \times 10 \times 10 = 20000$ ft-lb; while in one operation the total is $5 \times 100 \times 40 = 20000$ ft-lb.

Conservation of energy. It is held that all forms of energy are interconvertible and that the total energy of a system, transferred wholly or in part to another system, remains constant. Otherwise stated, energy is indestructible.

Thus in coal-derived electricity:

> *Coal* is *burnt* to provide the *heat* to raise the *steam*, to *drive* the *turbines* that *operate* the *generators* that *produce* the *current* for the *heat* of *electric fires.*

The sum of the energy of the electric fires and that of the inevitable losses at each stage must be that of the potential energy of the original coal.

Power. This is defined simply as the rate of doing work. The standard unit and, in this case, also the SI unit, is the watt, symbolized by W, and which may be defined as 1 J/sec.

This unit is named after James Watt (1736–1819), to whom is ascribed, in the modern sense, the invention of the steam-engine; he also invented the manner of stating the power of engines in terms of horse-power. One horse-power is 33000 ft-lb/min or 550 ft-lb/sec. Up to quite recently the power of the internal combustion engine was stated in horse-power, but this is now almost completely replaced by cylinder capacity.

However, since the past lingers on:

$$1 \text{ W} = 1 \text{ J/sec} = 10^7 \text{ ergs.}$$
$$1 \text{ h.p.} = 746 \text{ Ws.}$$

Mechanics

This is defined as that part of physics which is concerned with the behaviour of matter when subject to the action of force. Therefore, since all machines are involved in this manner, the study of the machines of any industry must start with elementary mechanics.

Levers. The lever is obviously concerned with force and matter although, or perhaps because, it is the simplest of all machines.

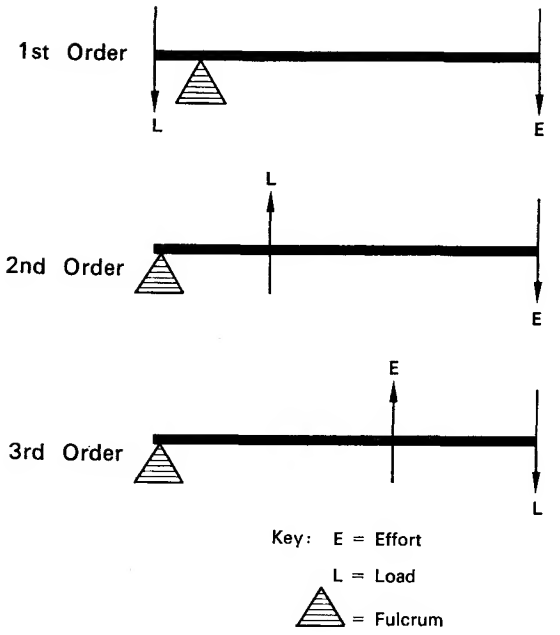


FIG. 4.3. Orders of levers.

Archimedes, the famous Greek mathematician who was born in Sicily about 287 B.C., is reputed to have said that, given a place for his fulcrum and a lever long enough, he could move the world—evidence, at least, of his knowledge of levers.

Levers are classified, almost by tradition, in three orders or classes according to the relative positions of the *fulcrum* or *pivot*, upon which the lever is moved, the *load* which is that upon which the force is intended to act and the *effort* which is the applied force (Fig. 4.3).

The most characteristic of the orders is the first, and this is usually selected for discussion. It will be noted that, in the remaining orders, the fulcrum is at the end of the system and that they differ in the positions of load and effort.

It is an interesting test of observation to attempt to discover the order applied to the many domestic and industrial small tools.

Moment of a force. Here the word 'moment' has a meaning associated with movement rather than with time; it is defined as a measure of the action of a force in causing the rotation of a body to which it is applied. Practically, a moment is the product of the force and the perpendicular or right-angled distance of its line of action from the axis.

This will be more easily understood by selecting examples using the action of a first-order lever (Fig. 4.4).

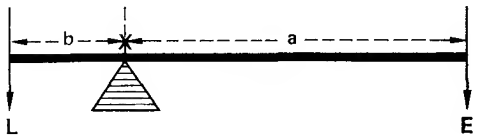


FIG. 4.4. Law of moments using a first-order lever.

(i) Given that E is a force of 10 kg and that a, the perpendicular distance from E to the axis, is 1·5 m, and that b is 0·5 m, find L, the load.
$a \times E = b \times L$. $\therefore 1{\cdot}5 \times 10 = 0{\cdot}5 \times L$;
$\frac{1{\cdot}5 \times 10}{0{\cdot}5} = L$. $\therefore L = 30$ kg.

This is the law of moments applied; it is evident that, given any three values, the fourth may be found.

(ii) Find the perpendicular distance from the axis of an effort of 5 kg which is necessary to achieve equilibrium with a load of 20 kg 10 cm from the axis.
$a \times 5 = 20 \times 10$. $\therefore a = \frac{20 \times 10}{5}$. The required distance is 40 cm.

The word 'equilibrium' is used above since the calculation establishes that the moments on each side balance. In practice, a slight

increase in either a or E or in both will result in the displacement of L.

The wheel. A wheel or disc which is rotated on its axle may be regarded as a number of levers, perhaps an infinite number. Mechanically it is an advance on the lever and it may be used to illustrate further matters which arise from the law of moments (Fig. 4.5).

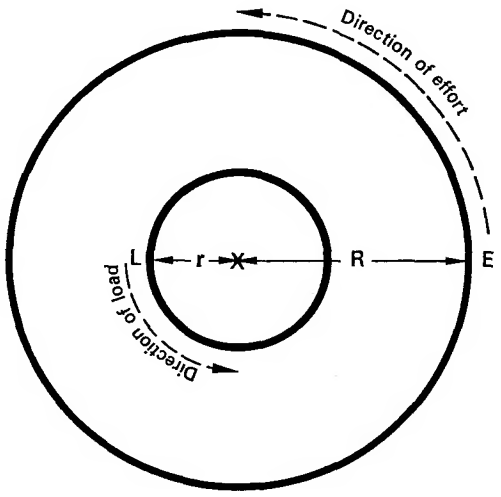


FIG. 4.5. A wheel in outline.

In Fig. 4.5, given that continuous energy is imparted to the wheel at its circumference and that the load is at the circumference of the axle, the moments of the system are:

$$E \times \text{radius of wheel} = L \times \text{radius of axle},$$

and, again, if numerical values are known for any three of these quantities, the fourth may be calculated.

Mechanical advantage. In the examples shown with the lever and the wheel, the load is greater than the effort (this is not necessarily always the case) and there is an appearance of gain which is termed

'mechanical advantage'; this is derived from the formula L/E, and in the examples (i) and (ii) under 'Moment of a force' above, the mechanical advantage is $\frac{30}{10}$ and $\frac{20}{5}$, i.e., 3 and 4 respectively.

In the wheel the greater radius is represented by R and the lesser by r. Transposing in the equation $E \times R = L \times r$, $L/E = R/r$, and thus the mechanical advantage may be calculated if the radii are known.

Velocity ratio. Although in the systems considered the load is greater than the effort, this must not be deemed as a contradiction of the law of the conservation of energy; to achieve this apparent anomaly the effort must travel further than the load.

In the example of the wheel the distances travelled may be set down as $2\pi R$ and $2\pi r$ respectively, using the formula to express the circumference of a circle; the relation between these quantities is known as 'velocity ratio' (VR); that is:

$$\text{VR} = \frac{\text{Distance travelled by effort}}{\text{Distance travelled by load}} = \frac{\text{D(E)}}{\text{D(L)}}$$

and in the example this is $2\pi R/2\pi r$ which becomes, on cancelling the similar factors, R/r.

Since the distances covered are travelled in the same length of time, the speeds of the components differ, and thus the use of the word 'velocity' in this context is justified.

Efficiency of machine. The operational value of any machine must be determined by the relation of the effort given to it and the work obtained from it; that is, efficiency $= \frac{\text{output}}{\text{input}}$. Otherwise stated this is

$$\frac{\text{Load} \times \text{Distance travelled by load}}{\text{Effort} \times \text{Distance travelled by effort}} = \frac{\text{L}}{\text{E}} \times \frac{\text{D(L)}}{\text{D(E)}}$$

$$= \frac{\text{L}}{\text{E}} \times \frac{1}{\text{VR}} = \text{MA} \times \frac{1}{\text{VR}} = \frac{\text{Mechanical advantage}}{\text{Velocity ratio}}.$$

Calculation of mechanical advantage, velocity ratio, and efficiency. Given that in a machine system the load is 100 kg and the effort

40 kg; the distance of travel of load is 1·5 m and that of effort 6·0 m, calculate the (i) mechanical advantage, (ii) the velocity ratio, and (iii) the efficiency of the machine, expressing the latter as a percentage.

(i) Mechanical advantage $= \frac{100}{40} = \frac{5}{2}$,

(ii) Velocity ratio $= \frac{6 \cdot 0}{1 \cdot 5} = 4$,

(iii) Efficiency $= \frac{\frac{5}{2}}{4} = 62 \cdot 5$ per cent.

In the matter and calculations above the influence of friction has been ignored. In practice a small addition to the effort is necessary to counteract this influence, but in the movements which establish velocity ratio, friction is not considered.

Pulleys. A single pulley is generally a device to change the direction of an effort; its velocity ratio is 1 and, if friction is neglected, its mechanical advantage is also 1.

A two-pulley system is illustrated in Fig. 4.6. Here, since the 2 kg load is divided to each side of the thread or cord while the 1 kg of the effort must function on each side of its pulley, the effort is in equilibrium with the load, friction being ignored. Thus the mechanical advantage is 2 and a slight increase in the effort will move the lower pulley upwards. It is possible to calculate the velocity ratio geometrically, but it is simpler and an interesting exercise to measure the movements of load and effort.

Rollers and gears. Figure 4.7 shows two rollers in contact; if the smaller is regarded as the driver and the other as the follower, and if the diameter of the former is 3 units and that of the latter 6 units, one revolution of the driver will turn the follower one half of its circumference since the velocity ratio is $2\pi R/2\pi r$ (the radii are a half of the diameters); this becomes $2\pi 3/2\pi 1 \cdot 5$, i.e. the velocity ratio is 2. (In effect this is the relation of the diameters.)

If the rollers are separated and a belt-drive substituted for

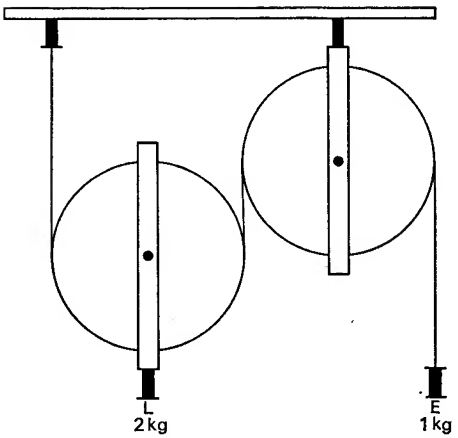


FIG. 4.6. A two-pulley system.

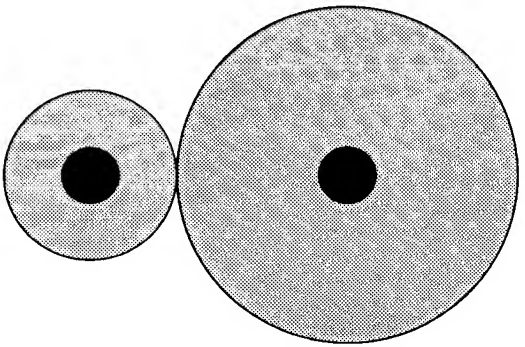


FIG. 4.7. Two rollers in contact.

contact, the ratio will be the same except that friction is likely to be greater.

The contact drive is rarely encountered, and in practice the action is usually transmitted by gears in which the teeth engage each other without the possibility of slip. In the design of the

gears the teeth project beyond the roller circumference, but the effective or pitch diameter is that of the roller.

The velocity ratio of the meshed gears may be calculated as in the previous models or by the number of teeth:

$$\text{Velocity ratio} = \frac{\text{Pitch diameter of follower}}{\text{Pitch diameter of driver}} = \frac{\text{Number of teeth of follower}}{\text{Number of teeth of driver}}.$$

In a chain-drive the movement is carried from driver to follower by a chain which engages the teeth; here friction is likely to exceed that of the direct gear, but in other respects calculations may be undertaken as before.

CHAPTER 5

Heat

Introduction. Heat is one of the many forms of energy. The heat of a substance is the internal energy, i.e., the force of movement of its molecules, atoms or ions. The differences in the physical states of gas, liquid, and solid are ascribed to differences in the form of this movement. In the first the particles move at random with continual collisions with each other and with the walls of any containing vessel. In a liquid the movements are restricted and tend to regularity, while in a solid the energy is expressed as vibration. Thus with the continuous addition of heat, most substances pass from solid through liquid to gas, the transitions from one state to another being usually observed as definite melting and boiling points. It is further apparent that the heat energy required to effect these changes varies very widely from one substance to another.

Temperature. The temperature is an expression or measure of the heat of a substance or, more specifically, of kinetic or internal energy. It is important to note that 'heat' and 'temperature' are strictly not interchangeable.

Measurement of temperature. Thermometers are the most familiar instruments for this purpose. They employ the property possessed by most substances of expanding with increase in heat. The thermometers in ordinary use contain mercury in a glass tube, but since this metal freezes at $-39°$ C, and temperatures below this are experienced in many parts of the world, ethyl alcohol with a freezing point of $-112°$ C, is used in very high latitudes or

altitudes, but its boiling point being 78° C its use is hazardous in hot climates. Mercury boils at 357° C, but this may be raised to about 550° C by filling the gap above the metal in the tube with carbon dioxide or nitrogen at high pressures to permit the examination of printing and other metals with relatively low melting points.

Stack thermometer. This blade-like PIRA instrument is designed to test the temperature within the paper stack. A temperature difference between newly delivered paper and its surroundings may result in the absorption of moisture with distortion of the edges of the stock which later conditioning may not wholly correct. The instrument operates by means of the expansion and contraction of a metal strip with changes in temperature—a principle common to many thermometers.

Pyrometers. The distinction between these instruments and thermometers is not easily stated, but in general pyrometers are used to measure temperatures greatly in excess of those possible with thermometers. Pyrometers may be classified according to the principles they embody; some of the more important are considered briefly below.

(a) *Optical* in which the quality and intensity of the light emitted by the heated body is used to indicate its temperature.

(b) *Thermoelectric* in which the principle of the thermocouple is applied; when wires of two different metals are connected at their ends an electric current passes through the circuit if the ends are at different temperatures. Thus when one end is placed in or by the heated body, the sensitive galvanometer or potentiometer incorporated in the system at the other end records the current or e.m.f. expressed as temperature.

(c) *Electric* in which the increased electrical resistance of a metal wire, usually of platinum, with rise of temperature is adapted to indicate temperature.

Temperature scales. The most important scale is Celsius or Centigrade. It was devised by the Swedish scientist A. Celsius (1701–44). The zero is the freezing point of water at normal barometric pressure (760 mm Hg) and it proceeds by steps to 100°, the boiling point of water also at normal pressure; the scale is extended

in each direction in equally spaced steps. The international authorities on standards insist on the use of Celsius, but Centigrade seems to be here for good; it is fortunate that the initial letters are the same. The scale is used over the greater part of the world for all purposes, but Fahrenheit still dominates the English-speaking lands in ordinary practice. Its freezing and boiling points of water are at 32° and 212° F respectively, and thus the steps are smaller than Celsius. The scale was the work of the German G. D. Fahrenheit (1686–1736), and it is often said that the zero at 32° F below water's freezing point represents the lowest temperature known to him, but it may, in fact, be specified by a standard mixture of ice and salt.

Conversion of scales. It will be observed that 100 deg C equals 180 deg F and that therefore 1 deg C $= \frac{9}{5}$ deg F and that $\frac{5}{9}$ deg C $=$ 1 deg F, but since 32° F $=$ 0° C a further adjustment is necessary. This is achieved in the conversion of ° C to ° F by multiplying the former by $\frac{9}{5}$ and then adding 32. For the change from ° F to ° C first subtract 32 from the ° F and then multiply by $\frac{5}{9}$:

As examples:

(a) Express 30° C in ° F: $(30 \times \frac{9}{5}) + 32 = 86°$ F.
(b) Express 59° F in ° C: $(59 - 32) \times \frac{5}{9} = 15°$ C.

It should be noted that in the majority of scientific text books Centigrade has become so conventional that the C is almost invariably omitted.

Maximum and minimum thermometers (Fig. 5.1). For some purposes a simple means of recording the upper and lower limits of temperature over a period is needed. In a maximum thermometer a small iron rod or index is pushed along the tube by the expanding mercury on rise of temperature, but when the liquid contracts the index remains in position to record the highest temperature reached; ethyl alcohol is normally used in the minimum thermometer—a similar index is carried below the surface of the liquid and when the latter contracts in a falling temperature the index moves with it, but on expansion the alcohol flows past the index to leave this to indicate the lowest temperature attained during the period of observation. These are often combined in

one instrument, the components being connected by a U-tube; the best known is Six's maximum and minimum thermometer. In all these instruments the index is returned to the starting position by the use of a magnet.

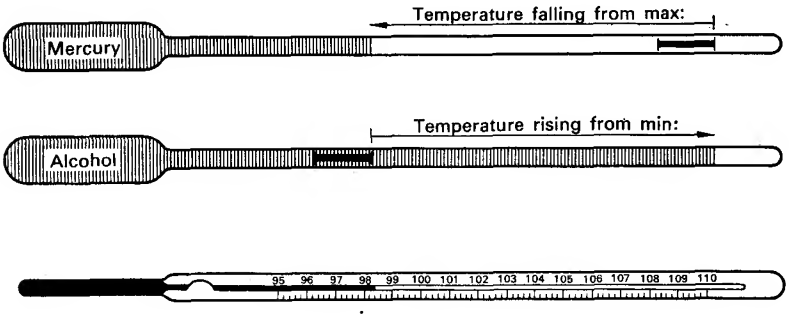


FIG. 5.1. Maximum, minimum, and clinical thermometers.

The clinical thermometer is a special type of maximum thermometer in which the expanding mercury passes through a capillary restriction placed a little above the bulb which prevents the return of the liquid on contraction. Therefore the maximum blood or body temperature—the normal is still expressed as 98·4°F —of the patient is indicated. The thermometer has to be shaken vigorously after use to return the mercury to the bulb.

Expansion of substances by heat. The use of the heat expansion of certain liquids for the determination of temperature has been considered above in brief but this almost universal property is of great scientific and technological importance.

(a) *Solids.* Expansion is largely attributed to the increase in the energy of vibration on rise of temperature with the consequence that the ions, atoms, or molecules demand more space. In solids, and particularly in metals, this expansion may be expressed as the coefficient of linear expansion, which is defined as the increase in length to any unit of length for a rise in temperature of 1° C. Thus total expansion is (length × coefficient × temperature rise) and,

given that the coefficient of linear expansion of steel is 0·000011, the expansion of a steel rod of 10 cm length subjected to an increase in temperature from 20° C to 30° C is (10 × 0·000011 × 10) cm, i.e. 0·0011 cm. or 0·011 mm.

TABLE 5.1. SOME COEFFICIENTS OF LINEAR EXPANSION

Aluminium	0·000026	Glass	0·000009
Brass	0·000019	Glass (Pyrex)	0·000003
Copper	0·000017	Platinum	0·000009
Iron (wrought)	0·000012	Steel	0·000011

While the linear coefficient is of greatest importance, since the surface and volume of a solid are also subject to expansion with heat, coefficients of superficial and cubical expansion have particular applications—among many others—in building and civil engineering.

(b) *Liquids.* The difficulty encountered in the determination of the heat expansion of a liquid is that the container is also increasing in size. It is evident that only expansion in volume is significant and, when that of the containing vessel is disregarded, the coefficient is stated as that of apparent expansion. The behaviour of water is anomalous: it contracts on cooling until 4° C is reached, but from that point downwards to the solid the liquid expands and ice itself has a lower density than water at that temperature. This phenomenon has very important consequences: ice is formed on the surface and it floats when free as in icebergs and floes; it has, indeed, been suggested that, if it were not for this property of water the ice would sink and the seas and oceans would be solid and life impossible. A minor hazard is the splitting of frozen water pipes at the thaw. This can only be prevented by the lagging of the pipes or by the use of a material which has sufficient elasticity to accommodate the expansion without fracture.

(c) *Gases.* Steam and internal combustion engines depend upon the power generated by the heat expansion of gases. The theoretical bases of this energy is expressed in the gas laws. (i) *Charles's law* states the relation between the volume of a gas and the temperature

—at constant pressure the volume of a given mass of any gas varies *directly* as the 'absolute' temperature (see below). (ii) *Boyle's law* states the relation between the volume of a gas and the pressure—at constant temperature the volume of a given mass of any gas varies *inversely* as the pressure. These laws are of very great importance in pure and applied physics and physical chemistry; they may be stated algebraically as:

(Charles) $V \propto A$; (Boyle) $P \propto \frac{1}{V}$; (Combined) $\frac{PV}{A} = C$, where

P = pressure, V = volume, A = absolute temperature, and C = a constant.

Absolute zero. It has been observed above that heat is an expression of the random or systematic movement of the particles of a substance and that the energy of this movement decreases as the temperature falls. It is therefore evident that eventually a point must be reached when this energy ceases altogether. Alternatively, Charles's law states that the volume of a gas decreases with temperature and it is reasonable to suppose that, again, a point must be reached when the volume of the gas will be negligible—it will be a solid or liquid. The point of solidification or liquefaction varies with the gas, but in a few—notably in helium—it is close to that point without kinetic energy; this is $-273°$ C or absolute zero. The temperature scale with its origin at this point is known as absolute or probably more usually as Kelvin in commemoration of the great physicist W. T. Kelvin (1824–1907).

In calculations involving temperatures and volumes of gases it is necessary to relate the former to 0° K.

As an example:—Given that a quantity of nitrogen at 10° C and 730 mm Hg pressure has a volume of 15·5 cc, calculate its volume at standard temperature and pressure (0° C and 760 mm). (Since the temperature is to decrease and the pressure is to increase, both influences will contribute to a decrease in volume.)

$0° \text{ C} = 273° \text{ K}$; $10° \text{ C} = 283° \text{ K}$ $(273 + 10)$.

$$\left(\frac{273}{283} \times \frac{730}{760}\right) \times 15{\cdot}5 \text{ (original volume)}$$

No.	Log
273	2·4362
730	2·8633
15·5	1·1903
	6·4898

No.	Log
283	2·4518
760	2·8808
	5·3326

Log	
6·4898	
5·3326	(subtract)
1·1572	

(antilog 14·36). Therefore the new volume is 14·36 cc.

Colour temperature. The Kelvin scale is becoming of rapidly increasing importance to the manufacturers of lighting equipment and to all industries in which critical colour matching and discrimination are essential. Printing is clearly among them.

When an iron bar is subjected to a continuous rise in temperature a point is reached where the metal begins to emit a dull red glow which changes to a brighter red and passes through orange and yellow to attain eventually a dazzling bluish-white a little before its melting point. From a study of Chapter 10 on Colour in this work it will appear that the spectral emission of the metal passes from the long wavelengths of visible radiation at the lower temperature to the shorter wavelengths at the higher. This must not be understood to imply that the radiation is necessarily confined to a narrow band of wavelengths but that the shorter become dominant as the heat increases.

The quality of an illuminant is expressed in terms of its colour temperature which is defined as that, in ° K, of a hypothetical black body which emits light of a spectral composition equal to that under examination. Some examples are given in Table 5.2.

It is important to emphasize that colour temperature indicates quality only and has no necessary reference to intensity. Thus it is possible to modify the colour temperature of an illuminant such as tungsten by filters. A blue filter raises the colour temperature but it is obvious that it also lowers the intensity.

British Standard for the Matching of Printed Colour, BS 950: Part 2: 1967, specifies a colour temperature of 5000° K for the illuminants used for the examination of printed sheet and original

TABLE 5.2. APPROXIMATE COLOUR TEMPERATURES (°K)

Colours of heated solids		Illuminants	
Very dull red	900	Candle	2000
Deep red	950	Tungsten filament	2800
Light red	1200	Carbon arc	4000–6000
Orange	1300	Fluorescent tubes	4000–7500
Yellow	1450	Sunlight	5500
Light yellow	1600	Blue sky	12,000–20,000

whether transparency or reflection copy (flat copy). The adoption of this standard is probably imminent in the United States. The BS specification also sets down a minimum intensity with recommended conditions of viewing.

For viewing during the run of the press, however, a higher colour temperature is desirable since the consequent increase in the blue component makes observation of the all-important yellow very much easier; the proposed US standard for this purpose is 7500° K; the BS recommendation is rather lower at 6500° K.

Quantity of heat. When water is brought to its boiling point by the heat generated during the chemical action of the combustion of gas or by the resistance of an electric element to the passage of the current, the statement that the temperature of the liquid is 100° C conveys no information on the quantity of heat necessary for the purpose since this quantity depends also on the mass of the water. There are many means of expressing this quantity; some are defined below.

The calorie. The quantity of heat necessary to heat 1 g of water through 1 deg C.

The kilocalorie. One thousand calories; this is also known as the great or large calorie; it is usually distinguished by the initial capital C while the smaller unit is written "calorie" with lower case initial.

The British thermal unit. The quantity of heat necessary to heat 1 lb of water through 1 deg F. It is usually abbreviated to B.t.u.

The therm. 100,000 B.t.u. (approximately 25,200 Cal.). A

practical unit to express quantity of heat. Domestic gas was earlier sold by volume, but this ignored the wide differences in heating value due to the character of the raw materials and the conditions of manufacture. The therm is the present unit for the purpose in the United Kingdom.

Specific heat. It is a matter of common observation that when a metal object and water are exposed together to the heat of the sun the metal reaches a high temperature very much more quickly than the water. This is to say, in other terms, that more heat is required to raise the temperature of a quantity of water than is required to bring the same quantity of a metal to the same temperature. The difference in the properties of these substances is stated in terms of their "specific heats". SH expresses a ratio and not a quantity: the ratio is referred to the SH of water which is given arbitrarily a value of 1.

Determination of specific heat. The methods in ordinary use are based upon the assumption that the heat lost by one component is gained by the other and, since water is normally selected for the former, the heat lost is its weight in grams stated as calories, the SH being 1. If small and fairly thick vessels of such metals as iron, copper, brass, and aluminium are obtained, the determination of the SH of these metals may be carried out without difficulty:

(a) The vessel is weighed and its temperature found. This will be close to that of the room.
(b) A measured quantity of water, preferably a round figure such as 10 g, is heated to a precise temperature and poured quickly into the vessel.
(c) The temperature of the water will fall rapidly, and when it is steady it is noted (the subsequent slow fall to room temperature is shared by water and vessel).

Given that the information obtained is: weight of vessel, 100 g; steady temperature of water and vessel, 40° C; initial temperature of vessel, 20° C; fall in temperature of water, 40 deg C; weight of water, 100 g; rise in temperature of vessel, 20 deg C; initial temperature of water, 80 deg C; the calculation is:

Quantity of heat loss by water:

Weight of water × SH of water × Temperature fall
$= 100 \times 1 \times 40 = 4000$ cal.

Quantity of heat absorbed by vessel:

Weight of vessel × SH of metal × Temperature rise
$= 800 \times X \times 20 = 16{,}000X$ cal.

Heat absorbed, $16{,}000X$; Heat loss, 4000 cals.

Therefore $X = \dfrac{4000}{16{,}000}$. SH of metal $= 0{\cdot}25$.

The same principle and method of calculation is applied in the use of the familiar copper calorimeter. This instrument, normally of 50 g weight, may be employed to determine the SH of most liquids and many solids; it is heat-insulated by cotton-wool or asbestos in a large can and, since the SH of copper may be taken for this purpose as the approximation 0·1; the 50 g calorimeter has a thermal capacity equal to 5 g of water.

TABLE 5.3. SOME SPECIFIC HEATS (WATER = 1)

Aluminium	0·21	Alcohol (ethyl)	0·55
Brass	0·093	Glass (common)	0·16
Copper	0·093	Glycerin	0·58
Iron	0·11	Ice	0·50
Lead	0·031	Paraffin (oil)	0·52

Latent heat. It has been stated above that heat is an expression of the internal energy of the particles of a substance and that the distinction between solid, liquid, and gas is due to the different forms of this energy.

When water is heated it will eventually boil, i.e. it will pass from the liquid to the gaseous state and however vigorous the action the temperature remains at 100° C, i.e. although the heat is being continuously applied, the thermometer reading remains unchanged. It is therefore reasonable to assume that heat energy is being used to effect the transition from one physical state to another. This energy is "latent heat"—in this case it is LH of vaporization.

The same process occurs in the changes from gas to liquid, from solid to liquid, and from liquid to solid, these being characterized by the LH of liquefaction, fusion, and solidification respectively.

Precise temperatures of boiling and fusion are criteria of purity, and they are consequently important in analytical chemistry. Since metallic alloys are not pure substances, the transitions from solid to liquid and the converse are marked, according to the nature of the components, by more than one period of temperature standstill. These considerations are of great significance in the theory and practice of the casting metals of printing; these matters are discussed in the appropriate chapter.

TABLE 5.4. SOME LATENT HEATS (in cal /g)

LH of fusion		LH of vaporization	
Aluminium	93	Alcohol (ethyl)	205
Copper	45	Carbon tetrachloride	46
Iron	49	Mercury	66
Lead	6	Water	539

Control of temperature. The most obvious control is exercised by turning the tap or switching off. However, more subtle devices are necessary for many purposes even if the effect is the same: these devices are thermostats. The simplest of these instruments employs (a) (Fig. 5.2) heat expansion and contraction of a metal to break and make an electrical contact or to vary the aperture through which gas passes to the jets as in the domestic stove: in the latter a preset temperature or heat number controls, by means of the thermostat, the gas inlet. Another simple device uses (b) differential expansion of metals such as brass and iron (see also Table 5.1).

In printing, thermostats have some applications in controlling

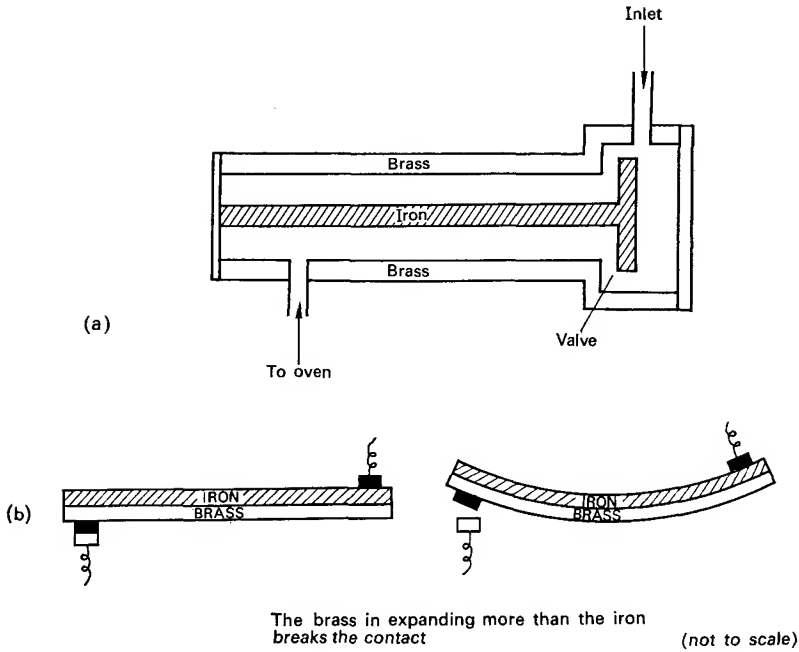


FIG. 5.2. Thermostats.

the critical temperatures of the synthetic adhesives used in bookbinding, but the most important function of these instruments is that of maintaining the temperature of the molten casting metals in general and more particularly those on the type-casting machines which have a tolerance close to $\pm$ 1° C.

The principle of the bourdon tube used in many pressure gauges has been adapted; this is a flexible metal tube containing mercury which expands under pressure or heat; this expansion is exerted at the spiral end of the tube which tends to flatten and in so acting turns a pointer to indicate pressure or temperature. When used as a thermostat the extension of the spiral moves a lever which tilts a glass tube also containing mercury; the liquid metal in its normal position connects two electrodes and the current passes to the

heater element, but when tilted the mercury flows to the other end of the tube and the contact is broken; when the temperature starts to fall below the optimum the spiral retracts, the lever withdraws, the tube resumes the normal position and the current again flows (Fig. 5.3).

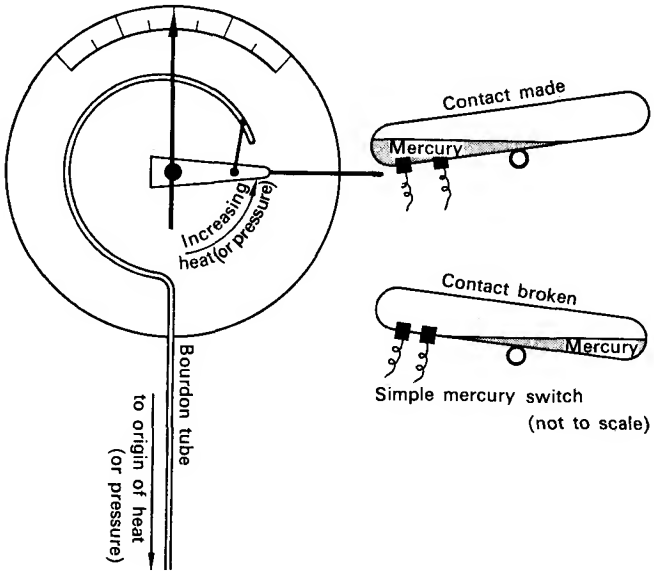


FIG. 5.3. Bourdon tube and gauge acting as a thermostat.

CHAPTER 6

Properties of Liquids

Introduction. A liquid exists in a physical state between that of a solid and that of a gas. The particles move with some freedom, but they are subject to the restraints of the mutual forces of cohesion, and thus this internal energy of movement is very distant from the random kinetic energy of the particles of a gas and from the systematic vibration of the particles of a solid.

Liquids take the shape of a containing vessel, but their compressibility varies from the very little to almost none—an obvious distinction to gases.

Surface tension. The mutual attraction or cohesion of the particles of a liquid imparts certain properties to the surface; the attraction within the liquid is exerted in all directions but, at the surface, one direction is free. The effect is best observed with small drops, in space or on a horizontal plane, which assume an almost spherical shape because these internal forces compel the liquid to adopt the form of the minimum area (the surface area of a sphere is less than that of a cube or other figure of the same volume). The slight departure from the true sphere is due to the downward pull of gravity. The effect of surface tension has been likened to that of a very flexible skin.

Each liquid has its specific surface tension; where there is little separation liquids are freely miscible as in water and ethyl alcohol, both with high ST; where there is wide separation the liquids are immiscible and mutually repellent as in water and oil. This latter

is the principle of the lithographic process which is considered in the appropriate chapter.

For many purposes in various printing processes it is necessary that a liquid, usually an aqueous solution, should wet the whole of a surface at once or without interruption. Examples are: photographic development of film or glass plate, some electrotyping solutions, and the coating with the light-sensitive solutions of the metal sheets in photoengraving and photolithography. To achieve this a "wetting agent" is added to the aqueous solutions to reduce the surface tension of the water. These materials are soaps in the chemical sense (see Chapter 13 and "Powderless etching", p. 290).

Surface tension falls with rise of temperature, and this is the reason—established long before the theoretical basis was known —for the much higher efficiency of hot water for cleansing purposes.

The force is usually expressed in dynes (the fundamental unit of force) along a straight line of 1 cm on the surface of the liquid under examination. While discussion of the various methods for the determination of surface tension are beyond the scope of this book it may be stated, in brief, that a very effective technique involves delicate weighing to determine the force needed to disrupt the apparent skin on drawing an edge (e.g. that of a microscope slide) through the surface.

Adhesion. In this context adhesion means the attraction between a liquid and a solid. A familiar example is the upward turn of liquids such as water where they meet the edges of a glass container which appears as a concave meniscus when the liquid is in a glass tube; the converse case is that of mercury where the meniscus is convex. In the former, the adhesive or attractive force between glass and water is greater than the internal cohesion, while in the latter the cohesive force is dominant.

Capillary action. If a capillary, i.e. a glass tube with a very small bore, is immersed in water at one end, the water will rise in the tube above the level of that in the container. This effect is to be ascribed to the same action as that which forms the concave meniscus considered above; the adhesion between glass and water is

greater than the cohesive force within the liquid. As may be anticipated, the converse action occurs with mercury—the metal level falls below that in the container.

This phenomenon is responsible for the obvious absorbent action of many papers, the extreme case being that of filter or blotting paper and the rather less obvious absorbent property of practically all papers. Printing ink passes into the interstices between the fibres, these spaces acting as capillaries.

Capillary action may be used as an alternative method for the measurement of surface tension since all the forces exerted may be assessed.

Vapour pressure. The greater part of the moving particles of a liquid such as water are retained at normal temperatures although a few are shot out from the surface. Since the application of heat accelerates the movement of the particles, this vapour pressure above the surface is increased. Thus more or less water vapour is taken into the atmosphere and the liquid is continuously evaporating.

Boiling. If the temperature of the water is raised progressively the point is reached when the evaporation proceeds violently and the temperature of the water ceases to rise whatever the quantity of heat. At this point the water is said to be boiling and, as is considered in Chapter 5 on heat, the heat energy is being absorbed in effecting the transition from liquid to gas. It is further possible to show that the boiling point is reached when the vapour pressure is equal to that of the atmosphere. This is quite general—a liquid boils when its vapour pressure attains the external pressure. It should therefore be apparent that the b.p. of water or any other liquid is related to the pressure on the surface. If the pressure is raised by applying some form of lid or cover while heating continues, the b.p. is also raised. This principle is used in the domestic pressure cooker—for which higher quality and speed are claimed as against the normal practice—and in the superheated steam-engine where the power available is greatly increased. If water is continuously heated in a closed system fitted with a pressure gauge (and a safety valve) it is possible to observe that, having raised the temperature much above the normal b.p., as the tem-

perature is lowered and the pressure reduced the b.p. of the water decreases step by step.

The converse may also be stated: the b.p. of a liquid is lowered by reducing the pressure by means of an exhaust pump; this action is the basis of distillation under reduced pressure, a process of great importance in manufacturing chemistry.

Refrigeration. Since the evaporation of a liquid absorbs heat, the temperature in the vicinity of a volatile—i.e. rapidly evaporating—liquid falls quickly. If ethyl alcohol or ether is dabbed on the forehead or back of the hand the chilling effect is very obvious; this is carried a stage further in the use of methyl and ethyl chlorides and some closely related compounds as local anaesthetics—a stream of the liquid from a container under pressure is directed to the skin covering the tissue being treated. The rapid evaporation, strictly boiling, freezes the tissue to deaden sensibility to permit the superficial surgery to proceed.

In large-scale refrigeration ammonia gas (NH_3—not the liquid commonly called ammonia which is ammonium hydroxide, NH_4OH) is compressed; the heat evolved is dispersed by radiation and/or water cooling; this is followed by expansion of the ammonia with fall of temperature well below the freezing point of water. In small-scale and domestic refrigation the principle is the same but the gas is ethyl chloride or other alkyl halide.

Many gases are liquefied by the same process—very high compression, cooling, and rapid expansion giving extremely low temperatures; indeed, elaboration of the methods has enabled a temperature close to absolute zero (— 273° C) to be reached in the laboratory.

Viscosity. It is obvious that liquids present great differences in freedom of movement. Water flows rapidly down a moderate slope while in similar conditions it may be difficult to detect the flow of a heavy oil; indeed, some substances which are liquids by definition, such as pitch and some high-grade letterpress printing inks, appear at first sight to be solids. These examples exhibit differences in viscosity which is defined as the internal resistance to movement in a liquid; it may be considered as an expression of

the degree of cohesion or of the ease or otherwise with which the layers of the liquid move relative to each other.

Measurement of viscosity. The poise (after the scientist Poiseville) is the unit in general use to express viscosity; it may be defined briefly as the resistance to movement between two parallel planes of a liquid separated by 1 cm; in more precise terms the force represented by 1 poise = 1 dyne sec/cm^2.

Direct determination of viscosity is difficult and therefore, for most purposes, comparion of two liquids is adequate, the viscosity of one being known.

Probably the most widely used method is the timing of the passage of the liquid through a capillary tube. In the Ostwald viscometer the instrument is filled with the test liquid to the level *A*. Then, by suction, the liquid is drawn round to fill the upper reservoir. The suction is released and the flow of the liquid between the levels *C* and *D* is timed on the stop-watch or clock. The instrument will have been calibrated previously with a control liquid, the viscosity of which is known. To avoid variations due to temperature change, the instrument may be suspended in a thermostatically controlled water bath.

Simpler instruments using much the same principle are available in which the outflow from a calibrated vessel through an orifice is timed similarly; it is unlikely that these are able to reach the accuracy of that considered above.

The falling-sphere viscometer is used to time the passage of a steel ball through the liquid under test. This is also illustrated in Fig. 6.1. It is, of course, apparent that this type of instrument cannot be used with highly pigmented fluids. The falling-rod viscometer replaces the small sphere by a steel rod which passes through a relatively narrow tube; this instrument is used for very viscous materials such as letterpress and lithographic inks in which the initial resistance to flow (or thixotropy) of the ink is broken down by movement of the rod in its tube before the test is undertaken.

Thixotropy. Many substances tend to become more viscous if undisturbed and, conversely, less viscous when disturbed by working or pressure. Thixotropy is very familiar in many types of

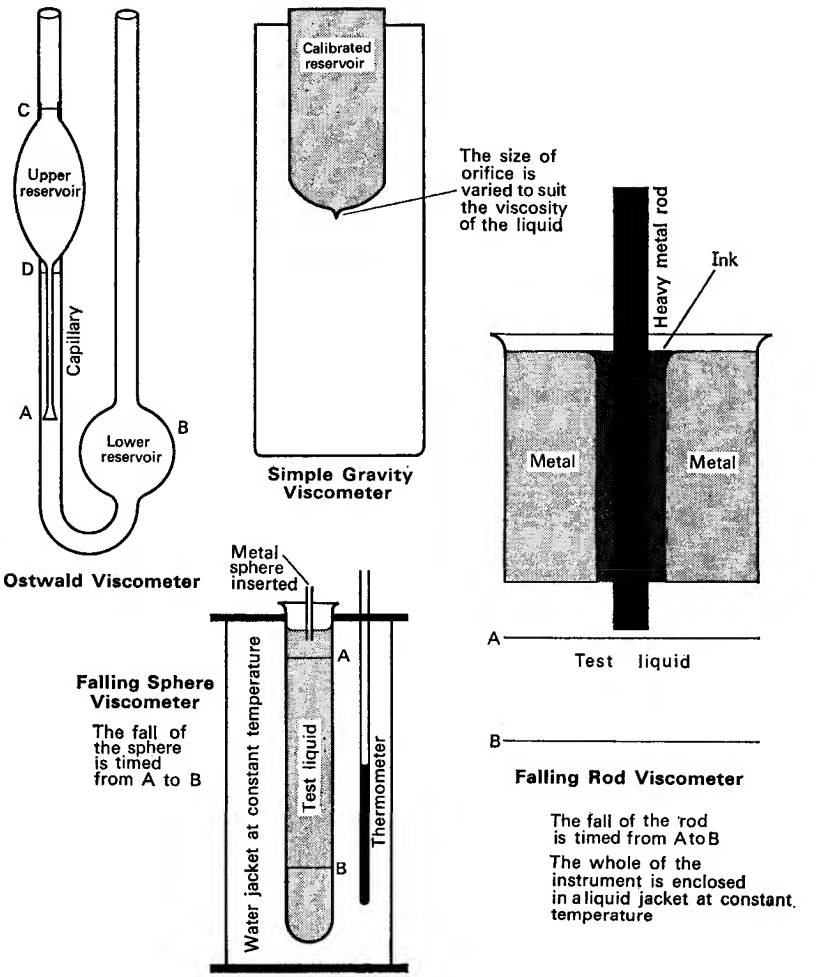


FIG. 6.1. Viscometers.

printing ink; these may appear as almost hard solids in the tins, but this character vanishes on the machine and the inks assume a more obvious liquid state.

Rheology. The study of the flow of materials and the deformations which may occur during this flow is clearly of fundamental importance to the printing industry. Rheology includes all the subjects briefly considered above: the viscosity of printing inks must be related to the printing process and thus to the manner in which ink is transferred to the image-carrying surface. Of almost equal importance are the varying viscosities of the adhesives used in bookbinding and of the metal coating solutions of the photographic processes.

Variations of the viscosity with temperature. With almost all liquids viscosity decreases enormously with rise of temperature, and for this reason it is necessary to control the conditions in which the viscometers considered above and all such instruments are used. The viscosity of water is cited in Table 6.1.

TABLE 6.1. VISCOSITY OF WATER AT DIFFERENT TEMPERATURES (poises)

Temperature (°C)	Viscosity	Temperature (°C)	Viscosity
0	0·018	50	0·0055
10	0·013	60	0·0047
20	0·010	80	0·0036
40	0·0066	100	0·0028

TABLE 6.2. SOME VISCOSITIES (all at 20°C in poises)

Substance	Viscosity	Substance	Viscosity
Benzene	0·0065	Glycerin	2·34
Ether	0·0023	Sulphuric acid (100%)	0·254
Ethyl alcohol	0·012	Toluene	0·0059

It is found convenient for some purposes to use the centipoise ($\frac{1}{100}$ poise) to state viscosity since whole numbers may be more convenient; for example, the viscosity of sulphuric acid in centipoises is 25·4.

CHAPTER 7

Atmosphere and Humidity

Introduction. The solid earth is enveloped in a gaseous ocean which, although in a very different physical state, is also part of the earth. The atmosphere at its lower levels is subject to many changes in condition—in pressure, temperature, and content, all of fundamental biological importance. At a lower stage of importance these changes influence many manufacturing processes: printing is among them.

Since the conditions of the external atmosphere have their consequences in the office or factory, the latter cannot be considered in isolation; the atmosphere is consequently discussed briefly below. The smaller scale industrial significance follows.

Extent of the atmosphere. The atmosphere is gaseous; it is therefore compressible and, under the influence of gravity, its density decreases upwards very rapidly. It is estimated that the lower 5 or 6 km (about $3\frac{1}{2}$ miles) has half of the total mass of the air, and at about 300 km (190 miles) it is so attenuated that this distance is usually considered the upper limit.

Atmospheric pressure. The vertical column of air obviously exerts a substantial pressure on the solid surface with which it is in contact. This pressure at sea level averages 1 kg to 1 cm^2 (nearly 15 lb to the square inch); at a height of 8 km (5 miles) this pressure is reduced to about half that amount. It is this diminution in pressure that is responsible for a great part of the difficulty of climbing in high mountains since it is almost impossible for the body to obtain enough oxygen without artificial aids; similarly,

it is necessary to pressurize the interiors of high-flying aircraft to an approximation of the conditions at ground levels.

Horizontal air movements from the gentle breeze to the hurricane result from differences in air pressure from area to area: the air flows from a zone of high to a zone of low pressure. It should be noted, however, that the variations in pressure at or near the surface of the earth are very slight compared with those at altitude although both are significant in meteorology.

Measurement of air pressure. If a jar of water sealed with a glass disc is inverted and one end immersed in a bowl of water and the seal removed, the jar remains full. This phenomenon is due to the air pressure on the exposed surface of the water in the bowl; it may, indeed, be shown that air pressure will support a column of water of at least 10 m long (33 ft). Variations in pressure are indicated by changes in the length of the column.

Such an instrument is too cumbrous in practice, but a column of mercury in a vessel of the liquid metal behaves in the same manner but, since the mercury is very much denser than the water, the column averages 760 mm at sea level and 0°C—this is standard or normal pressure at normal temperature; the apparatus is the mercury barometer.

This pressure expressed in dynes (trimmed to a round figure) is 1 bar, and the millibar ($\frac{\text{bar}}{1000}$) is the meteorological unit of atmospheric pressure chosen because it is small enough to make subdivision unnecessary.

The aneroid is an instrument much less bulky than the mercury barometer; it is also rather less accurate in general. It depends upon the rise and fall, with variations in air pressure, of the flexible lid of a partially air-evacuated box or drum; these movements are transmitted by means of a delicate lever system to the pointer on a dial. The recording aneroid barometer or barograph sets down pressure variations on a paper strip moving round a clockwork actuated drum.

The altimeter is an adaptation of the aneroid which is used to record the height of aircraft in terms of the changes in barometric pressure.

Air pressure applied. Some forms of pump directly employ air pressure; among these is the simple apparatus used to raise water from below for domestic and many industrial purposes; the cylinder of the pump is partially exhausted by manual or mechanical means and the subterranean water rises to fill the gap from which it is expelled by the opening of a valve.

In printing the most obvious use of this pressure is in the vacuum frames which ensure intimate contact during exposure between sensitized metal and negative or positive in the processes of graphic reproduction; pressure is reduced in the space between the rubber blanket and the glass front of the apparatus by a suction pump and the pressure reached, assuming an approach to complete exhaustion, is of the order of 1000 kg on a square of about 32 cm side (almost 1 ton/ft^2). The suction fingers of the paper feed apparatus on the press function by reducing the pressure within the finger while the normal external air pressure retains the paper as it is carried forward.

The baths and vats used for containing the acids of graphic reproduction, the electrolytes of electrodeposition, and the processing solutions of large-scale photography may be emptied by means of taps, but these are subject to corrosion or other chemical action with consequent lowering of efficiency; siphons are often preferred. One end of a tube filled with water is immersed in the liquid to be discharged while the other end leads to the receptacle; the latter and the end of the tube are positioned below the level of the bottom of the bath. Air pressure on the surface of the liquid together with the weight of the column of water in the pipe are sufficient to maintain the outward flow until the bath is emptied.

Composition of the air. Air is a very complex mixture of gases; its principal components are nitrogen and oxygen, the former being about four-fifths of the whole by volume and the latter one-fifth. The inert gas argon is present to almost 1 per cent with much smaller quantities of the other inert gases. The air also contains variable amounts of carbon dioxide and many of the oxides of nitrogen and industrial effluents such as sulphur dioxide and hydrogen sulphide; water vapour is present in quantities

which range from the infinitesimal over regions of extreme aridity to as much as 4 per cent in the tropical rain forests.

Temperature of the atmosphere. There are obvious variations in air temperatures in the horizontal sense; these differences are determined primarily by the relative positions of the earth and the sun. In the northern hemisphere the earth's axis is tilted towards the sun in the summer while, rather paradoxically, our planet is at its greatest distance from that source of heat. At the height of summer in the southern hemisphere the earth is at its nearest to the sun but, again, its axis is inclined to present the south aspect in the direction of the sun. Thus the seasonal variations between summer and winter result from the differences in the angle at which the sun's radiant heat is received, and temperature may be roughly related to latitude.

The vertical aspects of temperature change may be set down in a simpler manner; the average lapse rate is a fall of 0·55 deg C for each 100 m of ascent (approximately 1 deg F per 300 ft) up to about 11 km (7 miles), beyond which there is little change.

Humidity of the air. Oceans with the adjoining seas occupy nearly 71 per cent of the earth's surface, and thus the atmosphere is in contact with a vast area of water even if the lakes and rivers are ignored. Air and water vapour constitute a solvent/solute system in which, as mentioned above, there are wide differences in the proportions of the parts. The air has most of the properties of normal solvents; most importantly its ability to accept water vapour into solution increases with rise of temperature; further, the solubility of water vapour in air increases with barometric pressure. Saturation is defined as that condition when the solubility of a solute in a solvent is a maximum in the given circumstances (page 201). The water content of air may be conveniently expressed in terms of weight per volume. Table 7.1 indicates the solubility of water in air in the stated conditions.

Dew point. This is defined in the simplest manner as that temperature at which liquid water is discharged from its saturated solution in air; in Table 7.1 a cubic metre of air at 16°C and normal pressure is saturated with a water content of 10 g; if the temperature falls even slightly below 16°C, water will be precipitated.

TABLE 7.1. APPROXIMATE SOLUBILITY OF WATER IN AIR

Volume of air (m^3)	Weight of water (g)	Temperature (°C)	Barometric pressure (mm (normal))
1	5	0	760
1	10	16	760
1	14	26	760
1	50	40	760

Rain. When air, heavily charged with water, passes to a zone of falling barometric pressure and/or falling temperature it will, as before, be discharged after reaching saturation. It is, however, known that the very small droplets of water are normally carried in suspension unless dust particles are present to act as nuclei on which the droplets may coalesce to form raindrops heavy enough to be precipitated. Dust, that is, minute particles of solid matter derived from wind-borne matter from the surface or from smoke and other effluents over industrial areas, is almost always available; indeed, it has been stated that 300,000 particles/cc is far from abnormal over cities. Attempts have been made with varied success to precipitate rain over arid regions by the discharge of smokes of silver iodide from aircraft.

Hail results from the freezing of the larger raindrops and sometimes the union of several drops when these pass through rising air at a temperature well below that of liquid water. Snow consists of very beautiful crystals or combinations of crystals formed by the direct freezing of water vapour, often at considerable altitudes.

Absolute humidity. This is a means of stating the water content of air, usually by weight per volume in any units; thus, from Table 7.1, 50 g of water to the cubic metre of air is an expression of absolute humidity: it is independent of temperature.

Relative humidity. This is of far greater statistical and practical importance than the former; commonly abbreviated as RH it is

defined as the relation, expressed as a percentage, between the water vapour actually present in a given mass of air and that which would be present in the same conditions of temperature and pressure in that mass of air if it were saturated.

Selecting a further example from Table 7.1, if 10 g of water represents saturation of 1 m^3 in the stated conditions, then 5 g and 7·5 g of water respectively represent 50 per cent and 75 per cent RH in those conditions.

Relative humidity may be said to stand for saturation deficit; this is clearly shown when it is set down as a formula:

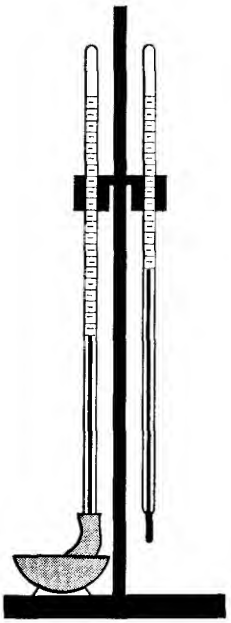
$$\frac{\text{Water content of given mass of air in given conditions}}{\text{Water content at saturation of same mass in same conditions}} \times 100 = \text{RH}.$$

Hygrometry. It is possible to determine absolute humidity by passing a measured volume of air through or over a water accepting substance such as 100 per cent sulphuric acid or anhydrous calcium chloride; the water content would be the difference in the weight of the substance used before and after the experiment. However, such a method would be tedious and expensive; it may also be almost valueless since, during the passage of time, the state of the air under consideration may have changed.

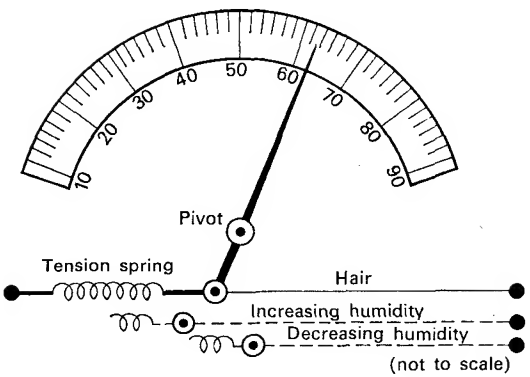
In practice, RH is determined instrumentally; the most important apparatus is the wet- and dry-bulb hygrometer, a simple form of which is shown in Fig. 7.1.

It has been set down in Chapter 5, under 'Latent heat', that heat energy is absorbed when a substance passes from the liquid to the gaseous state; consequently the temperature in the vicinity falls. In the present context the evaporation of water is advanced or retarded inversely as the water content of the surrounding air; in the extreme case of a RH approaching 100 per cent, evaporation almost ceases with the result that human beings become uncomfortably hot since the cooling mechanism of perspiration is largely ineffective.

In the hygrometer (Greek *hygros*, 'wet' or 'fluid') under consideration the bulb of one thermometer is free while that of the other is enveloped in muslin or similar absorbent material with



A simple wet and dry bulb hygrometer



A hair hygrometer

FIG. 7.1. Hygrometers.

the lower end of the textile immersed in water. Air temperature is indicated by the dry-bulb instrument while that of the wet bulb is reduced by the evaporation of the water. The difference between the bulbs is referred to the hygrometric tables published by the Meteorological Office in the United Kingdom or those of the United States Weather Bureau and similar institutions.

The efficiency of this simple hygrometer is increased if the air circulation is accelerated by fanning; in the 'whirling hygrometer' the pair of thermometers are carried in a wooden frame which is rotated around the handpiece.

The principle of an evaporating liquid is employed in more complex instruments such as the Regnault and Daniell hygrometers in which the water is replaced by the very volatile diethyl ether.

Most fibrous materials of animal origin expand with increasing humidity. Human hair lengthens by as much as 2½ per cent during an increase in RH from zero to the maximum. This property is used in the hair hygrometer the simple mechanism of which is illustrated in Fig. 7.1; another application of the same principle is in the Swiss weather toy in which the man comes out when rain is threatened while the lady appears when sunshine is due.

An industrial application of the principle, the sword hygrometer, is used to assess the RH of the air enclosed in piled or stacked materials, including paper.

Seasonal humidity. It may appear at first sight to be paradoxical that the absolute humidity of the atmosphere in regions of oceanic climates such as Atlantic Europe is greater in summer than in winter; this is explicable because the warmer air accepts more water, but it is important to observe that this does not necessarily influence RH.

Air conditioning. Apart from the demands of human comfort, many industrial processes are worked more efficiently when the air of the workroom or factory is maintained as nearly as possible at a fixed temperature and RH. Among the first industries to accept some kind of air conditioning was cotton, sections of which need high humidity; indeed, it was established in Lancashire,

partly because of the proximity of Liverpool but also on account of the notoriously damp climate of that county.

Air is fully conditioned when it conforms very closely to predetermined levels of temperature and RH with exclusion of dusts and smokes. Humidity may be controlled by passing the filtered air over aqueous solutions of given vapour pressure and raising the temperature as required or by lowering the air temperature almost to that of the freezing point of water, saturating it with water and then raising the temperature to the level needed. When the external air is very humid, RH may be reduced by lowering the temperature below the dew point, thus expelling some of the water, and then increasing the temperature. It is relatively simple to warm incoming cold air in severe weather, but attention must be given to the consequent need to adjust the RH.

In the extreme climatic changes between summer and winter in North America air conditioning apparatus is widely installed in shops, offices, factories, and restaurants and even in buses and private cars.

Humidity and printing. Paper is very hygroscopic. In absorbing water, it is subject to considerable variation in dimensions; when the absorption is uneven, as between the edges and the centre of a stack, the paper may frill or pucker irregularly. All this is to state the case for air conditioning in the appropriate sections of the industry.

The subject is considered more fully in Chapter 20, on 'Paper'.

CHAPTER 8

Magnetism and Electricity

MAGNETISM

Introduction. The discovery of a magnetic substance is usually believed to have occurred in the classic world near one or other of the two cities named Magnesia in Asia Minor, and this is acceptable at least as the origin of the name. Prior discovery is, once again, attributed to the Chinese and set back 2000 years more.

The substance is lodestone (or loadstone), i.e. magnetite, an oxide of iron with the formula Fe_3O_4. The common name is supposed to be connected with the idea of 'leading', since a suspended fragment will always move to point in the same direction, a property that was certainly used in navigation in the fourteenth century and probably much earlier.

Magnetic materials. Magnetism is a property possessed, or which may be imparted to, very few materials; these are principally iron (including steel) and its companion elements of group 8 of the periodic table, cobalt and nickel (see Chapter 11) and by some alloys of non-magnetic metals—Heusler's alloys of copper, aluminium, and manganese.

Properties of magnets. If a bar magnet is freely suspended by a thread at its centre it, like the lodestone, always turns to point in a fixed direction and if rotated through 180° it will again return to its original direction. Such an experiment suggests that there is some difference in the opposed ends of the magnet and, indeed, it may be easily shown that the direction sought by one end of the magnet is almost due north while the other end is attracted to the

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south; consequently the magnet is said to possess north-seeking and south-seeking poles, usually abbreviated to north and south and indicated by the initials. Here it is necessary to observe that the magnetic north has a slow drift and that it is now situated in Arctic Canada; consequently there are only two lines on the globe in which there is coincidence of magnetic and geographical north poles. In England the variation results in an angle of about 11°W in the position of the north magnetic to the north geographical pole.

It would be reasonable to suppose that, since the ends of a magnet have different polarities, if a magnet is divided the effect would be two magnets—one north- and the other south-seeking; however, this is not the case, and the separated parts behave exactly as the original bar. The process of division may be repeated with the same results—it remains impossible to isolate a north or south pole, and it must be accepted that if division could be continued to the limit, polarity would be shown by the individual atoms or molecules.

While the exact nature of magnetism may not be fully understood, it is possible to assume that the ultimate particles of a magnet, or many of them, are in strict alignment while those of a non-magnet may be disposed at random.

Two easily demonstrable properties of magnets are of great importance. (a) Like poles are mutually repellent while unlike poles are mutually attractive, and (b) the lines of force in a magnetic field are symmetrical with an origin at a north pole and a movement to a south pole.

The latter may be shown experimentally. Place a sheet of stiff paper over a bar magnet and scatter fine iron filings thinly and evenly on to the paper surface; tap the edge of the paper carefully to allow free movement of the filings. It will be observed that patterns are formed which indicate the lines of force in the conditions of the experiment; different patterns will appear when two magnets are used with (i) opposed polarities, or (ii) similar polarities and the power of the magnet or magnets in the crowding or otherwise of the curves. In Fig. 8.1 the lines are very much reduced in number for clarity.

While lines of force on a plane have been considered above, the magnetic force is exerted in all directions in space around the magnet.

The magnetic property tends to leak away, and thus bar magnets are protected by placing them in separated pairs with north and south poles in opposition connected by a small iron strip or keeper; in a horseshoe magnet the keeper seals the open end.

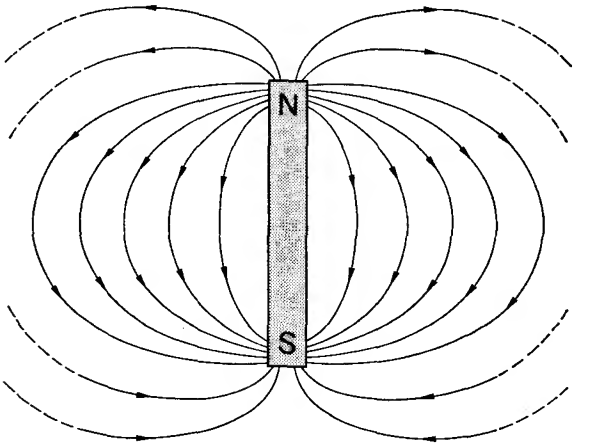


FIG. 8.1. Magnetic lines of force.

Induced magnetism. When an iron nail or rod is placed in contact with one pole of a magnet it becomes magnetized and will attract other iron objects; the same effect is produced, but at a lower intensity, if the rod does not actually touch the magnet. If the rod is soft iron its induced magnetism is lost on removal from the magnetic field, but steel retains the force and thus this metal is commonly used for permanent magnets.

Since induction precedes attraction it is evident that only those metals capable of being magnetized are attracted by a magnet.

Electromagnets. A permanent magnet may be prepared by repeatedly stroking a steel bar by either of the poles of another

magnet, but this method is not particularly efficient since the induced magnetism is of low power.

When an electric current passes along a wire a magnetic field is produced around the wire; this effect is used in the electromagnet (Fig. 8.2). If an insulated conductor is coiled round an iron rod to form a solenoid, the iron is magnetized when the current flows through the circuit; if the iron is replaced by steel a permanent magnet results the power of which is determined, within limits, by the duration and magnitude of the current.

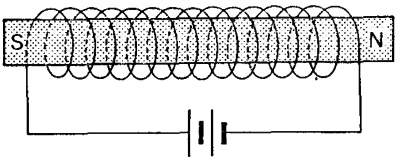


FIG. 8.2. Electromagnetization.

ELECTRICITY

Introduction. It must have been observed long before records were possible that when many dry materials are rubbed or brushed they acquire the property of attracting fragments such as fluff and dust. Greek observers noted that the effect is very apparent when amber, a fossil resin, is rubbed with a dry cloth, and thus this is not only a record of an electrical phenomenon but also the birth of a name—the Greek *electron* means 'amber'.

The definition of electricity is still a matter of some difficulty, and it is remarkable that the foundations of the science and technology of the subject were laid down in the later eighteenth century and in the first quarter of its successor at a period of almost total ignorance of its nature. Today electricity may be defined as a force or as energy set up when one area has an excess of electrons while another has a deficiency. (The reader is referred to Chapter 11, p. 176, which introduces the structure of matter.) Here it may be stated that while the electron is said to be 'negatively charged' the nature of that charge is still held to be uncertain.

In terms of the definition attempted above, the zone of excess electrons is deemed to be of negative charge while that of electron deficiency is of opposite sign—it is of positive charge.

There are many classifications of electricity according to its form, manifestation, or application, but for the present purpose these are reduced to three: (a) static electricity, (b) current electricity, and (c) electronics.

STATIC ELECTRICITY

This is defined, perhaps rather too briefly and consequently with some lack of accuracy as electricity at rest on or in a non-conducting material. It has been observed above that the attractive power imparted to amber by friction was probably the earliest recorded experiment in electricity. The discharge of electricity as lightning has long been a phenomenon of static on the grand scale, but its serious study is comparatively recent.

If an ebonite rod is rubbed with a dry piece of flannel it will attract small fragments of paper. When the experiment is repeated and the rod is suspended at its centre by a thread, another similarly treated rod of the same material will repel it; if, however, a glass rod which has been rubbed with silk is substituted, ebonite and glass are found to be mutually attractive.

The friction has transferred electrons from the flannel to the ebonite and the latter becomes negatively charged; the converse has occurred between the silk and the glass and the glass is positively charged. It follows that the textiles receive charges of opposite sign to their respective rods.

These experiments, in demonstrating the existence of static, also provide evidence, so important in these fields, that like repels like while unlike charges attract each other.

The electroscope. This is a very effective instrument for the study of static. In perhaps its most familiar form it consists of a brass disc or cap with a metal rod attached to its centre. Two strips of gold leaf are suspended, face to face, at the lower end of the rod; the rod and gold leaves are enclosed in a rectangular container with two opposed sides of glass while the others and the base are metal, the metal being earthed. At its entry to the con-

tainer the rod is supported by an electrically non-conducting material (Fig. 8.3).

When an electrostatically charged substance such as the ebonite mentioned above is brought close to or lightly in contact with the brass disc, a charge of opposite sign to that of the ebonite is passed to the metal and thus to the gold leaves since the metals are conductors. The leaves, having been similarly charged, are mutually repellent and they consequently move apart. If at this point the charged glass rod of the earlier experiments is placed near

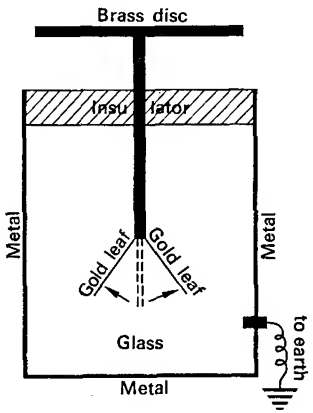


FIG. 8.3. An electroscope.

the disc, the charge is neutralized and the leaves resume contact. In the same manner, if the brass cap is touched with a finger the charge will be lost since the body, as a conductor, provides a path to earth.

The purpose of the earthing of the electroscope is to shield the instrument from external electrical influences other than those under observation.

Where the sign of a charged material is known the character of other charges may be determined since like charges reinforce the separation of the gold leaves while, as shown, the converse appears with unlike charges.

Printing and static electricity. Static is produced on a non-conducting surface by friction, pressure, release of pressure, and even by mere contact. All these influences are present with paper, normally a non-conductor, as it moves from feed to delivery, and consequently trouble due to static is well known in the industry; this applies particularly to both sheet- and reel-fed letterpress and intaglio machines, while it is at a minimum in lithography. With intaglio printing, fire is an additional hazard since the vapours from the volatile solvents of the ink may be spark-ignited if the generation of static is abnormal.

In the matter above dealing briefly with some theoretical aspects, the need for dry conditions for the experimental demonstration of static electricity has been stressed. The reason is that damp materials or surroundings provide means for the rapid discharge or even the prevention of static.

It therefore follows that where the usually recommended relative humidity of 65 per cent is maintained, the trouble may be all but absent; hence also the comparative immunity of lithographic printing.

The water content of the paper itself is important: at or above about 6·5 per cent static is little in evidence, and while there appears to be some difference of opinion on a more or less safe lower limit, about 4·5 per cent may be regarded as a mean.

In normal conditions coated papers are less liable to receive or generate static than others, while chemical and mechanical wood products are considered to be more affected than good quality rag papers.

Electrical elimination of static. Since it must be accepted that static is likely to be encountered in certain conditions, various improvisations have been devised, and more sophisticated apparatus invented, for its discharge or, as far as possible, its prevention; some of these are outlined below.

(a) *Earthing of machine.* The machine frame should be efficiently earthed in order that the charged paper, on contact with any metal component of the press, may leak at least some of its static.

(b) *Tinsel.* Aluminium or other metal foil is loosely wrapped round a wooden pin or rod often with a number of free ends

suspended downwards; the foil is earthed at its ends and the whole device is suspended above and just out of contact with the moving paper. This simple apparatus is believed to function in the following manner. The charged paper produces a charge on the tinsel which in turn ionizes some of the surrounding air; ions of the appropriate, i.e. the opposite, sign being attracted to the paper neutralize the static. In paper making the combination of friction and heat in the closing phases inevitably results in static which is largely countered by a method close to that given above—thin copper wires, supported by an earthed metal bar, are suspended in near contact with the moving paper.

(c) *High-pressure electrical ionization.* High voltage alternating current is carried to needle-pointed wires placed just above the paper to create both negative and positive ionization in the atmosphere around. Thus either sign of static on the paper is neutralized. It should be noted that the dangers are more apparent than real since the apparatus uses low voltage raised by a transformer and the current consumption is minimal.

(d) *Radioactive ionization.* Radiation also produces a zone of ionization, and for this purpose a very small amount of a radioactive material is carried in gold foil and shielded by heavy lead except where it is directed to the paper. Here again the dangers may be discounted given correct installation and operation. This method is said to be particularly suitable for use with plastics since most of these materials are all but completely water-free and thus very susceptible to static.

Electrostatic printing. Remarkable electrostatic processes have been evolved, primarily for the duplication of documents, and these have become serious competitors of the long established methods of photocopying. The most important of these processes is xerography, from the Greek *xeros*, 'dry'. This depends upon the property of certain substances, electrically non-conducting in the dark, which become conducting on exposure to light. The most used of these photoconductors is selenium, an element close to sulphur in many of its chemical and physical properties. The process also rests upon the effect already considered in which an electrostatically charged surface attracts another of different sign

or induces a charge of opposite sign by friction or contact—the triboelectric effect.

The stages in the process, which may be varied to achieve different purposes, are given briefly.

(a) A metal plate with a layer of selenium is subjected to a corona discharge produced by the high electrical potential on wires supported above the plate; in the ionized atmosphere the selenium becomes positively charged. This action takes place in the dark or in non-actinic light similar to that of a photographic darkroom.

(b) The charged plate is exposed to light in contact with a drawing on translucent material or to light from an original on a camera copyboard; in the latter, enlargement or reduction is possible.

(c) The area which receives the light, i.e. the non-image, becomes electrically conductive, and its charge passes to the metal support. The image remains charged, and it is often described as "latent" on the analogy of that of photography.

(d) The plate is dusted with a resinous powder of negative charge in a coarser carrier material; the powder attaches itself to the positively charged image.

(e) A sheet of paper is placed in contact with the powder image and the whole subjected to the corona discharge or spray. The powder is transferred to the paper since the charge is now greater on the paper than on the selenium. The powdered image is fused in low electric heat or infrared radiation. The sequence of powdering and transfer may be repeated, but the original electrostatic image on the selenium is progressively weakened.

It was apparent from the inception of xerography that it might well be the basis of another printing process, and today many rotary machines which embody the principle are in use. While these, perhaps, do not at present seriously compete with the standard methods, they are in course of continuous development.

The use of xerography to produce offset "masters" is already well established. The unfused powder image on paper of (e) above may be electrostatically transferred to a prepared zinc,

aluminium or paper plate on which it will form, again by fusion—a permanent lithographic image.

Electrostatic colour proving. In this remarkable adaptation of electrostatics a static charge on prepared paper is discharged by exposure to light through the yellow printer screen positive of an offset litho set; yellow pigmented particles attach themselves to the undischarged image. The process is repeated for the magenta, cyan, and black printers in succession, strict register being, of course, ensured.

The result is a colour impression of extraordinary quality which is achieved because each colour is an exact rendering of its half-tone positive.

Electrostatic ink transfer. It has been held for several years that electrostatically assisted transfer of printing ink from image-bearing surface to paper should offer many advantages.

Research to that end, applied to rotogravure, has been carried to a successful stage. An electrostatic charge is given to the impression cylinder carrying the paper with the effect that the ink is more freely transferred to the paper with decided improvement in quality, particularly on rough stock.

Tentative studies into similar applications to letterpress have been reported, but it does appear that the use of water makes the principle inapplicable or, at least difficult, in offset lithography.

CURRENT ELECTRICITY

In one familiar sense a current is a movement of water in a channel such as a river under the pressure of the water at the higher levels towards the source; there are here some analogies to the flow of electricity.

An electric current may be defined as a flow of electrons under the pressure resulting from an excess in one zone through or around a channel formed by a metal wire to another zone of electron deficiency. This is electricity as it is best known.

The generation of electricity. The production of static electricity by friction or pressure has been considered above. Two principal means for the generation of current are (a) chemical action, and (b) electromagnetism. These are briefly discussed.

(a) Chemical Action

It is shown in Chapter 11 that chemical action—combination, decomposition, the erosion by acids and alkalis, and the many others—involves the transfer of electrons, and during this transfer the electrons are momentarily free and they may in many cases be caused to flow through an electric circuit. The reader is referred to the chapter mentioned for more complete consideration of this subject.

The voltaic cell. When two dissimilar metals such as copper and zinc are immersed in dilute sulphuric acid the acid will attack the zinc but the copper is practically immune—this is among the dissimilarities. The acid in solution is an electrolyte, i.e. it is an apparent conductor of electricity, and it is dissociated into charged particles—the positive and negative ions:

$$\underset{\text{Sulphuric acid}}{H_2SO_4} \rightleftharpoons \underset{\text{Hydrogen ions}}{2H^+} \qquad \underset{\text{Sulphate ion}}{SO^{=}_4}$$

Each hydrogen ion has a deficiency of one electron and it is consequently of positive charge; the sulphate ion carries two excess electrons and is thus negatively charged. Atoms from the surface of the zinc become ionized in the solution and, since two electrons from each are retained by the metal, each zinc ion has two positive charges.

In the action the hydrogen ions move to the copper, the negative electrode; the sulphate and zinc ions form zinc sulphate and if the plates are connected externally or internally by a wire the excess electrons of the zinc will pass to the copper and thence to the hydrogen ions which become atomic and then molecular hydrogen (Fig. 8.4).

The voltaic cell described is far from efficient since, while some of the liberated hydrogen escapes at the surface of the electrolyte, bubbles of the gas collect on the copper and eventually the action ceases. In practice, oxidizing agents are added to the acid to remove the hydrogen as it is formed. The dichromate cell is an important example in which the powerful oxidizing agent potassium dichromate is present and a plate of the almost inert carbon replaces the copper.

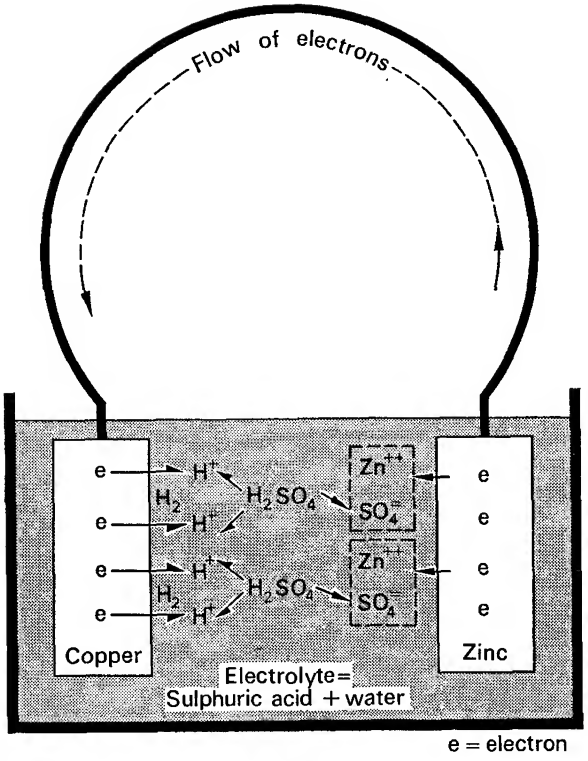


FIG. 8.4. A voltaic cell.

The leclanché cell. This is by far the most important of the cells of commerce. It consists essentially of a carbon cathode surrounded by manganese dioxide and crushed carbon with a zinc anode. The action has close analogies with that of the cell above: the electrolyte is ammonium chloride (salammoniac) which reacts with the zinc to form zinc chloride, leaving excess electrons on the metal; the ammonium radicle reacts with the manganese compound—also a powerful oxidizing agent—to give water while the ammonia evolved goes into solution. It should be observed

that, in spite of common usage, the single unit is a cell; when two or more of these are connected, the whole is a battery.

The dry cells and batteries used in portable radio sets and lamps are of the leclanché type; the electrolyte is in the form of a paste and evaporation is almost inhibited since the whole system is sealed.

The lead accumulator. The source of the ignition of most internal combustion engines is the accumulator or storage battery. In its earliest form it consisted of a pair of lead plates immersed in dilute sulphuric acid, and its action may be considered as very like that of the primary cells outlined above but with the very important difference that it is freely reversible.

The chemical process is rather complex and it is therefore convenient to set down the action on one plate in the simplest manner as it would occur in the cell above:

$$\underset{\text{Lead}}{Pb} + \underset{\text{Ionized sulphuric acid}}{2H^+ + SO_4^{=}} \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \underset{\text{Lead sulphate}}{PbSO_4} + \underset{\text{Hydrogen}}{H_2}$$

Again, positive lead ions combine with the negative sulphate ions to give lead sulphate, while the excess electrons pass through the circuit to the hydrogen ions and molecular hydrogen is formed.

In present practice the lead plates are cast as grids and a paste of lead sulphate is carried in the interstices.

During discharge the withdrawal of the sulphate results in the lowering of the density of the electrolyte while the reverse occurs in charging; therefore it is possible, by the use of an appropriately calibrated hydrometer, to ascertain the condition of the battery. Further, since the water is subject to electrolysis during the action and is lost as oxygen and hydrogen, it is necessary to maintain the level of the electrolyte by the addition of distilled water.

Each cell of the accumulator gives an e.m.f (see below) of a little more than 2 V, and thus, in use for car ignition, three or six cells are necessary for the 6 V or 12 V required.

The lead accumulator has a very high weight-to-power ratio, and less weighty apparatus, using light metal electrodes often in alkali electrolytes, has been long sought and success frequently claimed.

(b) Electromagnetic Generation

A relationship between magnetism and electricity has been suggested earlier in this chapter. It was shown that if a current is passed through an insulated wire surrounding an iron bar, magnetism is induced in the bar. In almost the same manner, when an electrical conductor is passed through a magnetic field an electric current is momentarily induced in the conductor. The existence of the current may be indicated by a galvanometer, an instrument used for the detection of very small currents without necessarily showing their magnitudes.

The generator. In the above example the current induced in the wire flows in one direction on entering the magnetic field and in the opposite direction on leaving; it is therefore an alternating current, usually set down as a.c.

This simple device is further developed. As shown in Fig. 8.5, a coil of wire, the armature, is rotated between the opposed poles of

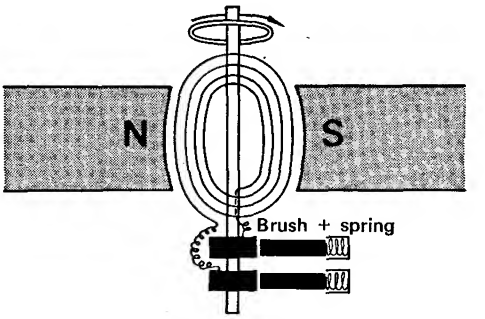


FIG. 8.5. A simple generator.

two bar magnets or between the poles of a horshoe magnet; the energy of the rotation is converted to an electrical current in the coil and, as will be apparent from the matter above, the current is alternating. The electricity is led away by two brushes, each in contact with a copper slip ring connected to the ends of the coil.

In the simple laboratory device, the brush is a strip of brass

which is carried lightly in free contact with the ring, but in more advanced apparatus, and particularly in large-scale commercial generators, it is a block of fine-grained carbon held in delicate contact by a spring.

The a.c. generator, or alternator, is in almost universal use. For direct current or d.c. generation, the slip rings are replaced by a commutator, which is a cylinder of insulating material sheathed in copper. The metal is divided along its length by grooves on opposite sides in such a manner that there is no contact between the parts (Fig. 8.6). In operation, the sections of the commutator are so connected to the coil that as the brushes pass over the sections the return half of the current is inverted and reinforces the first half to give what is in effect a direct current.

FIG. 8.6. A commutator.

The d.c. generator is usually known as a dynamo.

In the apparatus in use by the public and commercial generating authorities, the permanent magnets mentioned above are, of course, replaced by very powerful electromagnets.

The principal electrical units. An analogy has been suggested above between the flow of water and that of electricity, and while it would be irrational to carry the parallels too far they still have considerable value.

Water contained in an elevated tank will flow out through a pipe to a lower level. The actual magnitude of the flow is a result of (a) the head of water in the tank the pressure of which is determined by the altitude and the volume of water. This may be stated otherwise as a difference created by variation in pressure at the two ends of the pipe. (b) The rate of flow is also a consequence of the diameter of the pipe: it is apparent that the smaller the bore the greater the restriction.

In electricity the variation at the ends of the system is the potential difference or p.d. which creates the pressure or, more usually, the electromotive force or e.m.f. which is expressed in volts. The conductor offers a resistance to the flow as does the pipe; this is stated in ohms, often written as the Greek letter Ω (omega). The flow itself is, in more precise terms, the current expressed in amperes, inevitably abbreviated to amps or A.

Electrical power is evidently the product of the current and e.m.f.; thus a current of 1 A at 1 V equals 1 watt (W). The watt is too small a unit for most purposes; the kilowatt hour (kWh), i.e. 1000 W maintained for an hour, is the standard unit of industrial and domestic consumption.

Definitions of these electrical units appear below.

Ohm's law. A relationship has been suggested between e.m.f., resistance, and current; and, in fact, this may be stated in quantitative terms. G. S. Ohm (1787–1854) showed in 1826 that, since resistance rises with temperature, given a constant temperature.

(a) I (current in amps) $= \dfrac{E \text{ (e.m.f. in volts)}}{R \text{ (resistance in ohms)}}$.

The components of this equation may be transposed:

(b) $I \times R = E$.
(c) $R = E/I$.
(The symbols are those ordinarily used in this context.)

Thus, given any two quantities the third may be calculated; for example:

(i) The e.m.f. is 100 V and the resistance 2 Ω.
Calculate the current.

Using (a): $I = \dfrac{100}{2}$, i.e. 50 A.

(ii) A car battery directs a current of 2 A through a lamp filament with a resistance of 6 Ω. Find the voltage.

Using (b): $2 \times 6 = E$, i.e. 12 V.

(iii) A small filament lamp takes a current of 0·5 A when connected to a 4 V battery. Find the resistance.

Using (c): $R = \frac{4}{0{\cdot}5}$, i.e. 8 Ω.

(iv) One bar of a domestic electric fire consumes 1200 W; the mains supply is 240 V. Find the resistance.

(Watts = volts × amps) $1200 = 240 \times$ amps (A)

$$A = \frac{1200}{240} = 5.$$

Current is 5 amps.

Using (c): $R = \frac{240}{5}$ $\therefore$ resistance is 48 Ω.

Experimental verification of Ohm's law. Using the circuit shown in Fig. 8.7 it is possible by the use of the variable resistance or by

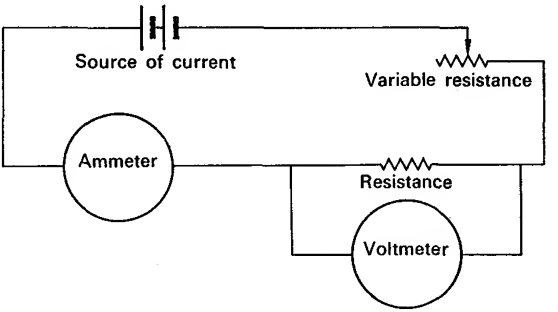


FIG. 8.7. Circuit for verification of Ohm's law.

raising or lowering the e.m.f. at the source (or both) to obtain data via the meters which may be tabulated to provide evidence of the validity of Ohm's law.

Units defined in terms of Ohm's law. Since the basic electrical units bear a relationship expressed by the law, they may be defined also in terms of that law. There are, however, more involved definitions applied to the ohm and amp to which the volt may be referred.

Ohm. That resistance of a conductor or circuit which, given a p.d. of 1 V across the ends, passes a current of 1 A. Alternatively, an ohm is the resistance at 0°C of a uniform column of mercury with a mass of 14·5 g and a length of 1060 mm.

Ampere. The current produced by an e.m.f. of 1 V through a resistance of 1 Ω. Alternatively, an ampere is that current which, passing through a solution of silver nitrate, liberates 0·001118 g of metallic silver per second. (See Chapter 17.)

Volt. That e.m.f. which causes a current of 1 A to pass through a resistance of 1 Ω. Since the ohm and the ampere are definable in the absolute terms set down above, this simple definition is fully adequate.

Series and parallel. All electrical appliances offer more or less resistance to the passage of the current, and consequently information based on Ohm's law is important for their installation; further, such appliances from lamps to motors are usually grouped. This grouping is classified in two types, and in any system one or other may be used or a combination may appear.

Series. In this system the appliances are connected in line in such a manner that the electricity passes in sequence from one to the next. In series the e.m.f. of the source is shared but the same current must pass through each component.

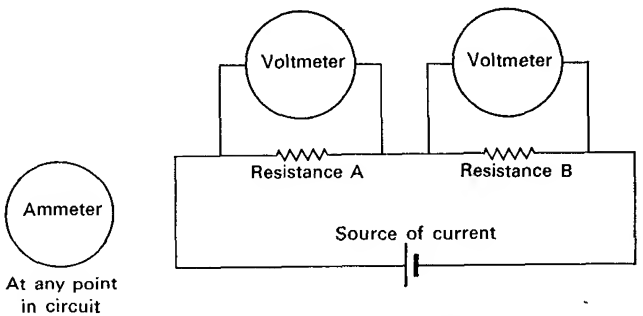


FIG. 8.8. Resistances in series.

In the circuit given in Fig. 8.8, the ammeter may be moved to any position to demonstrate the unvaried current, but the

record of the voltmeter at each resistance will differ if they are unequal:

(a) The total e.m.f. is E; $E = I \times R$; I = the fixed current.
(b) $E = (I \times R_A) + (I \times R_B)$.
(c) (Since $E = I \times R$) $(I \times R) = (I \times R_A) + (I \times R_B)$.
(d) (Dividing throughout by I) $R = R_A + R_B$.

Otherwise expressed, the total p.d. across resistances in series is the sum of those across each resistance. (It should be observed that resistance in this context means any electrical appliance.)

The above may be applied to any number of resistances in series; for example:

Given a current of 5 A through a circuit in series with five resistances of 4, 5, 6, 8, and 10 Ω respectively, calculate the total e.m.f.

$R = 4 + 5 + 6 + 8 + 10 = 33\ \Omega$. Since $E = I \times R$,
e.m.f. $= 5 \times 33 = 165$ V.

Parallel. In a circuit in which the resistances are connected in parallel the lead-in is branched to be re-united at the further end of the system. Thus the current is shared while the p.d. is uniform, this being the converse of that of a circuit in series. Reference to Fig. 8.9 will indicate that an ammeter is connected to each resistance while a voltmeter bridges the whole.

Using the symbolism as before:

(a) $I = I_A + I_B$.
(b) $E = I \times R = I_A \times R_A = I_B \times R_B$.
(c) $I = \dfrac{E}{R}$; $I_A = \dfrac{E}{R_A}$; $I_B = \dfrac{E}{R_B}$.
(d) $\dfrac{E}{R} = \dfrac{E}{R_A} + \dfrac{E}{R_B}$ [substituting (c) in (a)].
(e) $\dfrac{1}{R} = \dfrac{1}{R_A} + \dfrac{1}{R_B}$ (dividing numerators by E).

This stated verbally is: the reciprocal of the total resistance is equal to the sum of the reciprocals of the separate resistances;

further, from the above, the same p.d. appears across each constituent of a circuit in parallel.

The substance of this may also be applied to any number of resistances in parallel.

Given an e.m.f. of 10 V and resistances of 4, 5, 6, and 10 Ω respectively, connected in parallel, calculate the total resistance and total current of the system.

$$\frac{1}{R} = \frac{1}{4} + \frac{1}{5} + \frac{1}{6} + \frac{1}{10} = \frac{15+12+10+6}{60} = \frac{43}{60}.$$

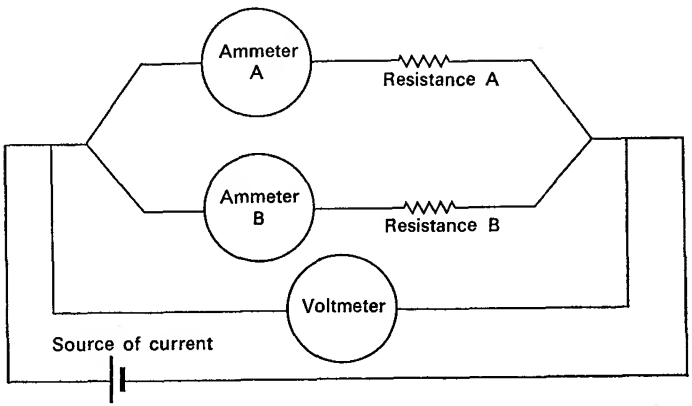


FIG. 8.9. Resistances in parallel.

Therefore total resistance is $\frac{60}{43}$ Ω.

$$\left(I = \frac{E}{R}\right) \quad I = \frac{10}{\frac{60}{43}} = \frac{43}{6}.$$

Therefore total current is 7·16 A.

Measuring instruments. A few of the simpler instruments are considered below. There are, however, some matters which are of general application:

(a) A meter must influence as little as possible the circuit in which it is used.
(b) The ammeter measures current. Since it is used *in* the circuit it has necessarily a low resistance (Fig. 8.10).
(c) The voltmeter is used to record e.m.f. and since it is connected in the manner shown (Fig. 8.10) it must have a high resistance.
(d) The operating principles of the ammeter and the voltmeter differ little other than in detail, but the position in the circuit (Fig. 8.10) must be maintained.

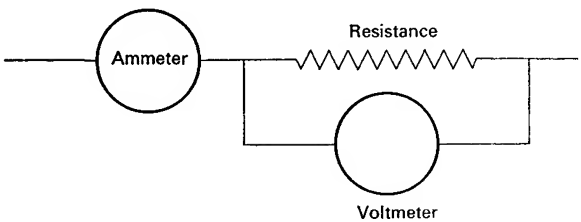


FIG. 8.10. The position of meters in a circuit.

Moving-iron meter. The current is passed through a solenoid and its magnitude influences the magnetic field and consequently the movement of the iron attached to a pointer. In the example shown in Fig. 8.11 a hair spring exerts a restraint on the otherwise too free iron.

Moving-coil meter. This is probably the best known and most efficient type of meter. The current is led through a coil placed between the poles of a permanent magnet; the magnitude of the magnetic field set up around the coil produces greater or lesser repulsion towards the field of the permanent magnet and the coil rotates accordingly. The too free movement of the coil is controlled by springs attached to the pivot, situated above and below the coil; these springs also act to carry the current to the coil (Fig. 8.12).

The galvanometer. This instrument is used for the detection of very small currents. It is rarely expected to indicate precise electrical units and its scale is marked out in fractions or percentages

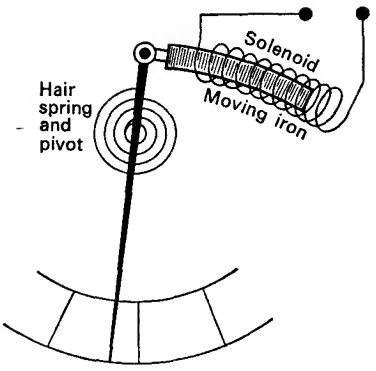


FIG. 8.11. A simple moving-iron meter.

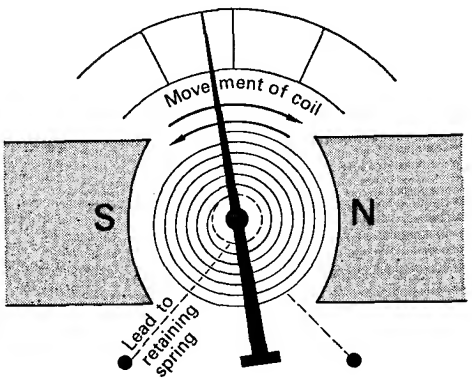


FIG. 8.12. A simple moving-coil meter (from above).

of an arbitrary whole. In perhaps the most familiar form of the galvanometer a coil which passes the current under test is delicately suspended between the poles of a permanent magnet. As in the instrument described above, the rotation of the coil is determined by the magnitude of the current. A mirror which is attached to the coil reflects the light from a small lamp as a disc to the instruments scale. The mirror galvanometer is a component of or is attached

to the spectrophotometers and colorimeters used in many industries, including printing, for the examination of colour.

ELECTRICAL APPLIANCES

Heating apparatus. In general, the conductivity of metals decreases with rise of temperature. This is very easily demonstrated during the experimental study of Ohm's law by heating part of the conductor with a Bunsen burner.

The corollary, i.e. that conductivity increases with falling temperature, is also freely demonstrable. It has, indeed, been long known that resistance to the passage of a current ceases at absolute zero (— 273°C), and striking advances in electrical generation and power are anticipated in apparatus immersed in liquid helium at a temperature close to that zero.

Electric heaters employ the heating effect of a current, and it is apparent that this effect is cumulative since rising temperature is accompanied by rising resistance.

The metals in use for the heater elements are alloys of chromium and nickel with some iron; these are suitably resistant and are almost free from corrosion.

Illuminants. All electric illuminants function because a solid or gas is made incandescent by the passage of the current.

(a) *Filament lamps.* These consist of a finely drawn tungsten wire in a glass container filled with more or less inert gases such as nitrogen and argon. The incandescence is another example of the heating effect of the current.

(b) *Carbon arcs.* These were among the earliest of electric lamps. They consist of carbon rod electrodes which are drawn apart by the passage of the current through a solenoid; white-hot carbon particles leap the gap between the electrodes to give arcs of high luminous intensity. In the enclosed type the carbons are protected by a glass envelope which, as well as affording a shield from draughts, also enclose during operation an inert atmosphere of carbon dioxide. Open arcs used cored carbons in which metallic oxides contribute to the luminous qualities of the flame. The enclosed type has greater ultraviolet emission and a higher colour

temperature. It is still widely favoured for photoengraving photography in monochrome and considerably for colour, and for metal printing. The open arcs find greater uses in the photolithographic process both for photography and platemaking. The photogravure process appears to be less exclusive.

(c) *Gas-discharge lamps.* These lamps consist of glass tubes containing freely volatilized metals, chiefly sodium or mercury, or inert gases, mainly neon, argon, or xenon. All the materials above are ionized by the passage of the current and all become incandescent although their luminous qualities differ substantially.

(i) *Sodium vapour lamp.* This illuminant provides the brilliant orange-yellow so popular for road lighting. It is useless for any ordinary photographic purposes since there is no red or blue emission.

(ii) *Mercury vapour lamp.* The blue–green light of mercury vapour is also used for public purposes and, since it has a considerable ultraviolet component, it is still employed for exposing the carbon tissue in the photogravure process and for monochrome process photography. However it, also, is almost totally deficient in red.

(iii) *Fluorescent lamp.* This is a mercury vapour lamp in which the inside of the tube is coated with a material which has the property of absorbing some of the ultraviolet radiation of the vapour and converting it to radiation within the wave band of visible light. Since there is a wide choice of substances with different properties, fluorescent tubes are available in a variety of colour emissions. These have extensive uses as industrial illuminants, and the qualities of some types are important in colour printing and colour matching (see Chapter 5).

(iv) *Xenon arc.* This is a high intensity discharge lamp using the inert gas xenon. The oscillations of a.c. produce a brilliant flash each half cycle which, with the standard 50 cycle source, gives 100 flashes per second, a frequency sufficiently high to be apparently continuous. The xenon

arc has found uses in process photography, including colour, and in printing on metal.

(v) *Iodine.* There are various types of iodine discharge lamp. The element is used with starter filament in a quartz tube or as a metallic iodide in glass. The light produced is of extreme intensity and, unlike some of the other apparatus mentioned, some of the containers are small enough for use as car headlights. These lamps are adapted to many photographic purposes and are being increasingly appreciated in process photography.

Fuses. A fuse is an alloy of low melting point which is part of a circuit. Its purpose is to protect the system from damage if, for any reason, a current too high for safety is being passed. The temperature rises with the current until the melting point of the metal is reached and the contact is broken. Fuse alloys are of copper, tin, zinc, and lead in various proportions although a single metal may be used if of a gauge fine enough. For large-scale installations, automatic contact-breakers replace fuses. These employ several diverse principles, among them that in which the rising current forms an increasingly intense magnetic field to the point at which an iron bar in the field is withdrawn and the contact broken.

Switches. The familiar domestic switch acts by forcing a metal strip or strips between grippers to make a snap contact. Heavier switches do little but extend this mechanism, but they may be single or, more likely, double pole, i.e. they engage one or both sides of the system.

For high-powered machines, including large printing presses, which use pressures greater than the normal mains supplies, these simple switches may be hazardous. In such cases contact is made by a push-button-operated electromagnet activated from a low voltage source; thus the operative is isolated from possible contact with danger.

Electric motors. At its simplest, the electric motor consists of an electromagnet and a coil or armature free to revolve in the intense field of the magnet. This apparatus is therefore yet another

development of Faraday's pioneer work in electromagnetism, and it does not differ in principle from many of the appliances considered above. The motor is, indeed, very close to the alternator and dynamo, but, while in the first the current is converted to mechanical power, in the generators this power is used to produce electricity.

There are great variations in the design of motors made necessary by the differing purposes which range from the continuous load of machines such as printing presses to the fluctuating power needed for much electric traction and the intermittent action of hoists. This vast field is obviously beyond the scope of this work.

ELECTRONICS

Introduction. It was once possible to define electronics, even then with some lack of precision, as "electricity in space" in distinction to current and static electricity. The word is now applied, however, to a wide variety of instrumentation for which this definition is inadequate or even inaccurate.

It is proposed to consider briefly below apparatus which is conventionally called electronic, much of which has printing applications.

Photoelectric cells. These instruments, also known as photocells, may be broadly classified as (a) those that emit electrons on the impact of light, and (b) those whose resistance decreases as the intensity of light received increases. Both types are used to vary the quantity of electricity passing through a system, the current being amplified if necessary.

Photovoltaic or barrier layer cell. This cell belongs to type (a) above. A metal plate is coated with a layer of selenium (some of the properties of this element appear earlier in this chapter), silicon, or copper oxide. This layer, in turn, has a metal deposit sufficiently thin to be transparent. When the upper and lower metal elements are connected, the reception of light creates a p.d. between the surfaces of the sensitive layer, and a current passes.

Photoconductor cell. This cell uses directly the property of selenium or other elements or compounds in which conductivity

varies as the light received. This, otherwise stated, is that resistance varies inversely as the light; thus this cell belongs to type (b).

Photomultiplier. This may be described as an extremely sensitive photoelectric cell which may be used for the detection of minute quantities of light. The photomultiplier consists of a number of pairs of electrodes—the cathodes and dynodes—in an air exhausted envelope. The electrodes are maintained at a p.d. of about 100 V and they are arranged in such a manner that light falling upon the first cathode ejects electrons which are accelerated to the first dynode, thence to the second cathode, and so on, being amplified

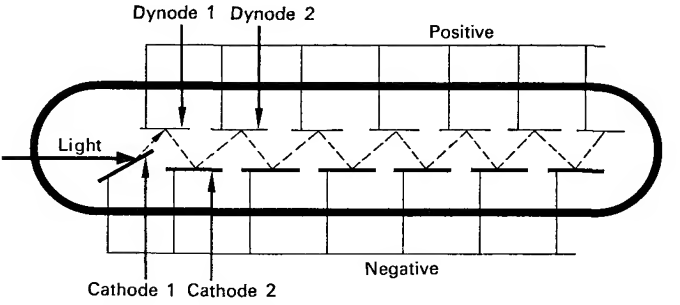


FIG. 8.13. A simplified diagram of a photomultiplier.

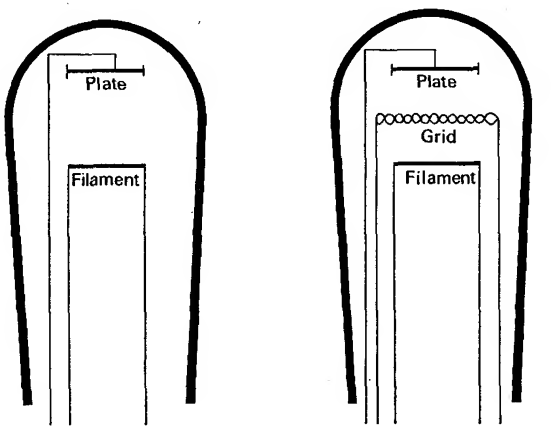
at each stage. The final result is an electric current of serviceable magnitude (Fig. 8.13).

Phototransistor. Certain materials such as germanium and silicon possess properties which are the reverse of those of metals; i.e. their electrical resistance increases with decreasing temperature until at absolute zero their conductivity is nil. These materials are semiconductors and they are used for the purpose under consideration with the addition of carefully controlled impurities.

The boundary of two different semiconductors in contact offers a barrier to the passage of an electric current, but if heat, light or, other forms of energy are directed on this boundary, the barrier effect is reduced in proportion to the energy and thus the flow of a current may be controlled. Transistors are used in a wide range

of light electronic apparatus where their low weight and small size has displaced valves (see below).

Thermionic valves or tubes. The simple two-electrode valve or diode consists of filament and a plate contained in an evacuated glass bulb (Fig. 8.14a). When the filament is heated by the passage of a current it releases electrons, and when the plate forms the anode, i.e. when it carries a positive charge, the electrons are attracted, but if the charge is negative the electrons are repelled.



(a) A simple diode valve (b) A simple triode valve

FIG. 8.14.

Therefore if a radio signal is directed through the plate, a half-cycle of the oscillations is cut out and the valve is acting as a detector.

In the triode valve a third electrode, the grid, is introduced between filament and plate (Fig. 8.14b). Fluctuations in the grid potential control the passage of electrons from the filament (or cathode) to the plate, and since much greater streams pass to the plate, the triode acts as an amplifier.

The valves in use are much more elaborate than those discussed although the principles remain. The plate is usually a nickel

cylinder which encloses the filament and grid, while many are available with four, five, and even more electrodes.

The cathode ray tube. In this device, familiar in television and the oscilloscope, an electron beam, proceeding from the cathode placed at the narrow end of the glass envelope enclosing a high vacuum, is directed towards the fluorescent screen at the viewing end. The anode of the system carrying a high potential is coated on the inside of the tube. The electron beam is passed through electromagnetic fields, the intensity of which are varied in sequence in such a manner that the focused beam scans the whole surface of the screen. The phosphors which give the image are metallic sulphides, oxides, and other compounds which glow on the impact of the electron stream or cathode ray. The television image is formed by variations in the intensity of the electron stream which result in related variations in the glow. Colour television employs three cathode ray guns which direct electrons, each to their specific phosphors, to give the red, green, or blue components of the image. These are the additive colours or physical primaries (see Chapter 10). The rays are isolated by the shadow mask, a sheet of perforated metal. The geometry of the system is such that the ray, in passing through an aperture in the mask, can only contact phosphors of the appropriate colour.

Electronics and printing. In view of its nature and its products it is hardly surprising that the electronic apparatus already widely used in the graphic arts and that being slowly adopted is concerned with light and colour. It should be observed that some of the devices discussed below have been long familiar in the processes of reproduction and it is, indeed, possible that it is in this field that most of the development to come will be achieved.

The densitometer. This instrument is employed primarily for the measurement of the density of continuous tone negatives and positives and the reflection density of originals such as photographs. It may also be used, with some reservations, to determine the integrated density of halftone at all stages—integration in this context means the uniformity which should result from the mixture of dot and surrounding space to give various greys. The densitometer consists essentially of a lamp which directs a small area of

light through a lens to the sample and thence to a photocell. The varying impulses from the cell are amplified and the density indicated on the dial. It is necessary to remark here that density is a mathematical concept, and readers are referred to Chapter 9 for

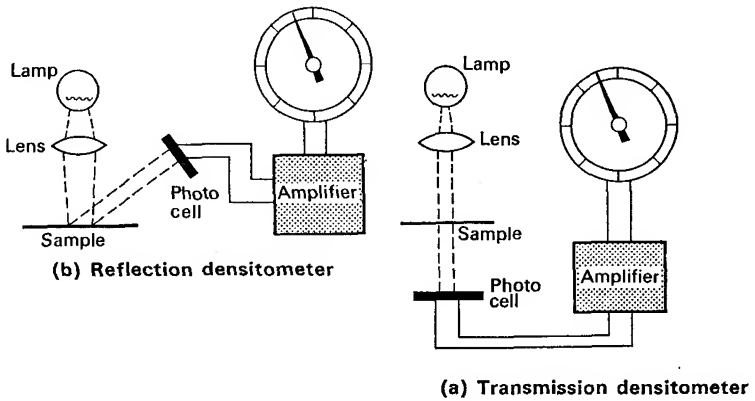


FIG. 8.15.

consideration of this subject. Most densitometers are primarily equipped to record transmission density, but all are provided with means of measuring reflection density (Fig. 8.15).

The light meter. All types of camera copyboard lamps are subject to fluctuations in intensity due to similar variations in the current. Therefore critical exposures cannot be purely a matter of time. The light meter is placed on or near the copyboard in such a position that it receives as closely as possible the same illumination as the original. The light falling on the meter passes through a photoelectric system and the time of the exposure modulated in such a manner that, if the intensity of the light drops, the time is increased and the converse; i.e. in other terms the quantity of light is measured and the time adjusted accordingly.

The spectrophotometer. At its most splendid and most expensive this instrument records graphically the spectral characteristics of the sample under examination in terms of wavelength and pro-

portion present at almost each wavelength to any desired accuracy, this latter being determined merely by the time of operation. However, abridged spectrophotometers are available. These instruments are equipped with a minimum of nine filters which cover between them the spectral range. In operation, the blue component of the sample is recorded through a filter at close to the minimum wavelength of visible light. The emission is passed through a photoelectric cell and amplification system, and its intensity is expressed as a percentage by means of a carefully calibrated galvanometer. The process is repeated through the range of filters ending with a red towards the long wave part of the spectrum. At each filter stage the system is set to a standard white, usually magnesium oxide.

The results are set down on a prepared graph and it is not difficult to interpolate a continuous line in the spaces between the filter records.

The spectrophotometer has uses in the critical assessment of printed colour, but it should be regarded as an instrument of the graphic arts laboratory rather than the workshop or machine room.

The colorimeter. This piece of apparatus measures the colour of a sample in terms of given colours. It is possible by the use of the appropriate filters to measure and express any colour as a quantity of each of the physical primaries—blue, green, and red —and although the latter need definition this implies expressing the sample in terms of trichromatism. If the filters are in accord with the specification of the Commission Internationale d'Éclairage system (see Chapter 10), the most precise statement yet possible of colour constitution may be achieved.

This instrument functions in much the same manner as that described in the preceding paragraph, but for the purpose above three filters only are needed.

The colorimeter may be said to have workshop applications since trichromatism is the foundation of most printed colour, but it, again, is more likely to be a tool in the laboratory.

Colour control on the press. It will be observed that the difference between the instruments in the paragraphs above and the densitometer is largely that of greater and lesser elaboration. If a filter is

interposed at the input end of the densitometer it is possible, with reasonable accuracy, to determine a colour component of a sample. Indeed, some of these instruments are provided with sets of trichromatic filters.

If a colour bar (a check strip), that of the magenta, is examined through a green filter by means of a suitably adapted apparatus, ideally it will appear as black provided that the ink is at full strength, and the densitometer will indicate little or no reflected light. If, however, the density of the ink falls and the white of the paper dilutes the colour, this will be recorded as more or less reflected light according to the degree of dilution. Similarly, if not so markedly, changes in the actual colour of the ink may be observed.

In the same manner the yellow, cyan, and black colour bars may be assessed during the run of the press.

It is necessary to note that the word "ideally" has been used since consideration must be given to the inherent inaccuracies of the inks and the probable difference in hue between a wet and dry colour. Further, while the extreme case of a filter has been cited which does not, in principle, transmit any reflection from the ink, it would be practicable to use other filters or to examine the colour bar without a filter.

There is little doubt that recognition of this photometric method of control is extending since precision in four-colour halftone is only attainable with standardization of the inks in proving and on the press.

Electronic colour separation. By far the greater part of the work entrusted to this apparatus consists of colour transparencies and, indeed, many reflection originals are converted to transparencies. Typically the transparency is wrapped round a transparent cylinder, and similarly sized cylinders carry the photographic films which will be exposed to form the yellow, magenta, cyan, and black printer continuous-tone positives or negatives. The five cylinders are rotated on a common axis and thus complete size uniformity is assured. Apparatus is, however, available which is capable of enlargement and reduction of the transparency and of producing halftone positives or negatives. It is probable that in most practice

the transparency is copied first to the required dimensions and then reproduced same size; direct halftones involve the interposing of a contact screen at some stage. Here, in the interests of lucidity, the Contone apparatus is considered. The stages are briefly set down below.

(a) The transparency is scanned from within the cylinder by a minute point of light; the normal choice of spacing for the scanning is either 1000 lines/in or 500 lines; the former takes twice the time.

(b) The point of light, coloured as its portion of the subject, passes through a system of prisms and/or mirrors and the beam is split into three parts. The split beams are directed to either a blue, green, or red filter, and therefore only the components of the original of these colours are separately transmitted to the next stage.

(c) The filtered beams pass to the photocells where the light energy is converted to currents which vary as the intensity of the light. The weak energy is raised to the required magnitude through photomultipliers and amplifiers.

(d) The emerging currents are divided, to be directed to (i) the colour computer, where the blue, green, and red emissions are modulated to be corrected as far as possible for the inherent errors of the printing inks, and to (ii) the black computer, where the colour emissions are modulated in such a manner that together they will ultimately express the original in terms from black to an attenuated grey. It is possible to obtain wide variations of the black printer to suit the character of the original.

(e) The modulated currents are passed to the lamps. The point of light from each varies in intensity from the maximum to almost nil and, consequently, the rotated photographic emulsions receive exposures which range from total to negligible during scanning. The scanning line should be so diffused as to be hardly visible.

All the extant apparatus will produce either negatives or positives according to the process for which they are intended (Fig. 8.16).

Electronic engraving machines. This apparatus is, up to the last stage, very similar in principle to the above. In the black and white machines the original, usually a photograph, is supported on the outside of a cylinder or on a flat table. Here it is scanned by the point of light; the reflected light passes through a photoelectric and amplification system and the character of the emergent current is usually subject to modulation under the control of the operator. In the final stage the cutting edge of a V-shaped tool is raised or lowered, as activated by the current, to engrave a half-

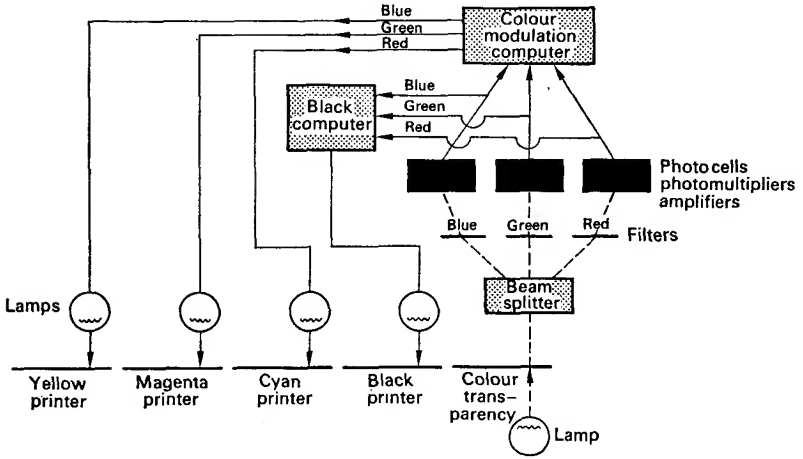


FIG. 8.16. Simplified diagram of electronic colour scanner.

tone structure on a metal or, more rarely, a plastic plate. Alternatively, as in one of the earlier machines, the point of a stylus is surrounded by a heater element and the temperature of the point is raised or lowered over a wide range as the current is modulated. The heated stylus point burns recesses in a plastic plate, which in some models is supported on a cylinder to result in a halftone structure in relief.

For colour the final stages are as in monochrome engraving while the intermediate processes of colour correction and black computation resemble closely those considered in the electronic colour-separation apparatus.

Photosetting. This rapiding developing apparatus uses a variety of electronic components combined with the applied optics and chemical processes of photography. The purpose is the preparation of positives, and sometimes negatives, of type matter. Since the production of photolithographic and photogravure printing plates is almost entirely applied photography, photoset material is particularly suitable for these processes.

However, in view of its very wide scope, consideration of photosetting must be omitted with great regret from the present work.

Electronic instruments for paper testing. It is held to be appropriate to deal with some of this apparatus in Chapter 20.

CHAPTER 9

Light: Optics

INTRODUCTION

There is little doubt that the most valued of the senses is sight and, while the industry is far from unique, printing itself makes critical demands upon vision and its products have no purpose unless they are seen.

Many in the classic world of thought held that things are known visually only when "light" is carried from the eyes to the object being observed and, although contested at the time in favour of what is virtually the modern view, this idea persisted until the twelfth century at least.

In attempting to define light an immediate difficulty arises: as commonly accepted, light is a quality which is felt or experienced and which, accordingly, cannot be known to those blind from birth. The physical scientist must primarily study the causes rather than the apparent effects even, indeed, if these are not experienced at all. For the purposes of this work the scientific aspect must be accepted in general although it is clear that printing is also concerned with the other view.

Light is therefore defined as that which is emitted by flames and other luminous bodies and that objects, not themselves luminous, are seen because they reflect light generated elsewhere.

THE ELECTROMAGNETIC SPECTRUM

There is, however, a more subtle and certainly more complex definition: light, or more precisely, that which is the cause of the

sensation called "light"—as discussed above—consists of radiant energy which occupies a very small part of that vast system of radiation called the electromagnetic spectrum. This system is a probably continuous series of wave motions or vibrations which travel through air at a velocity of about 300,000 km (186,000 miles) per second and at reduced velocity in denser media such as water or glass. The waveforms of this radiation oscillate at right angles to the direction of motion and the extraordinary differences in the character of the radiation is ascribed solely to differences in wavelength.

Wavelength is measured from crest to crest or from one position on a wave to the equivalent on its neighbour (Fig. 9.1).

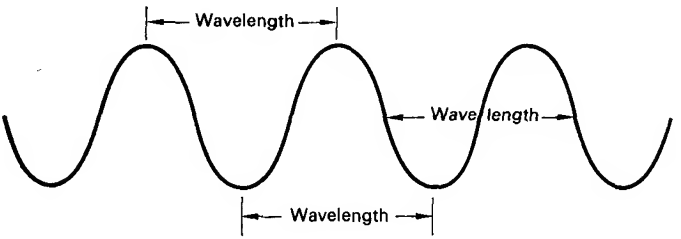


FIG. 9.1. Wavelength.

Human eyes respond to that portion of the scale with a wavelength range which may be expressed in one or other of the units below:

(1) μ (micron), $\frac{1}{1000}$ mm.

(2) mμ (millimicron), $\frac{1}{1{,}000{,}000}$ mm.

(3) Å (ångstrom), $\frac{1}{10{,}000{,}000}$ mm.

No. 2 will be used in this work. (The S.I. unit is the nanometre (10^{-9}m).)

Visible light has then an approximate wavelength range of 400–700 mμ, approximate since there are variations between individuals

and differences in the same individual with health or sickness and fatigue.

The known gamut of radiation is at its minimum in the cosmic rays, originating in outer space, with wavelengths of the order of a ten millionth of a millionth of a millimetre through, very briefly and of increasing magnitude, X-rays, ultraviolet, light, infrared, heat, television, radio, to reach wavelengths of 1000 m onwards.

The near neighbours of light—ultraviolet and infrared—are of great importance in photography, particularly the former; the effect of the extension of human sensitivity into these regions has been frequently discussed—it is, indeed, suggested, not without challenge, that the result would be an amazing richness of experience.

Frequency is an alternative to wavelength which is often or even usually employed in fields outside the present matter. It may be defined as the number of vibrations per second. Thus it can be calculated by dividing the velocity by the wavelength. In the case of the type of radiation under discussion, e.g. given a wavelength of 1000 m the frequency is 300,000 km ÷ 1000 m, i.e. the frequency is 300,000.

It should be observed that, while movement of radiation in air is assumed for many purposes, it appears that these wavemotions do not demand any medium for their propagation as was once supposed.

Small differences in the wavelength range of light have a very important effect—a change in wavelength results in a change of colour. This topic, of profound interest in printing, will be deferred to the next chapter; here, for most purposes, light is assumed to be achromatic, i.e. without colour.

OPTICS—THE BEHAVIOUR OF LIGHT

Path of light. Light is said to be "propagated in straight lines"; this may easily be confirmed if a simple opaque shape is interposed between a source of light and a reflecting surface. However, it ought also to be noted that light is readily diverted from the straight and narrow path by the several means discussed below. Thus the

phrase should be amended perhaps by the addition of "unless it is diverted".

The pinhole camera is very little in evidence today, but it may be used to illustrate the straight or rectilinear movement of light; a light-tight box has a thin metal foil pierced by a needle or fine drill, centred at one end; at the opposite side is a ground-glass

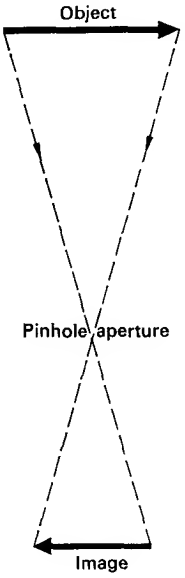


FIG. 9.2. The principle of the pinhole camera.

screen or a holder for a photographic plate. If a brilliantly illuminated object is placed symmetrically in front of the pinhole at a distance of a few feet, an inverted image will be seen on the screen or will appear on the photographic plate after a somewhat prolonged exposure followed by development. The reason for the inversion of the image is that light, travelling from the extremities of the object, crosses at the aperture (Fig. 9.2).

While this camera is without the defects of many equipped with lenses, it is rarely used; prolonged exposures are necessary on

account of the very small aperture, and the image tends to be a little diffused especially if the pinhole is larger than it should be.

Shadows. Unless the light source is extremely small the shadows cast by an opaque object appear in two forms. First, there is an area of total absence of light, the umbra, which may have a more or less sharp margin according to the distance of the illuminant.

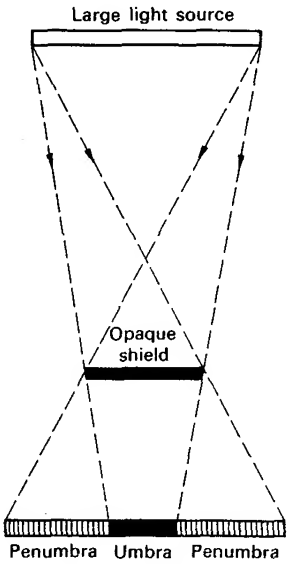


FIG. 9.3. Umbra and penumbra.

Secondly, there is an area in the form of a fringe, the penumbra, around the total shadow where the light is only partially intercepted. The formation of umbra and penumbra may be explained by considering a fairly large illuminant. The rays from its extremes will pass over the edges of the obstruction while an area in the centre will be subject to a total eclipse (Fig. 9.3).

Inverse square law. The intensity of any radiation may reasonably be expected to decrease with distance from the origin. Assuming

in the case of light a point-source from which the energy is moving in all directions and further assuming that it is allowed to fall first on an area of one metre square placed at 1 m from the source and then on an area of 2 m square at a distance of 2 m. The quantity of light received on the two surfaces will not be related as the simple distance but as indicated in Fig. 9.4.

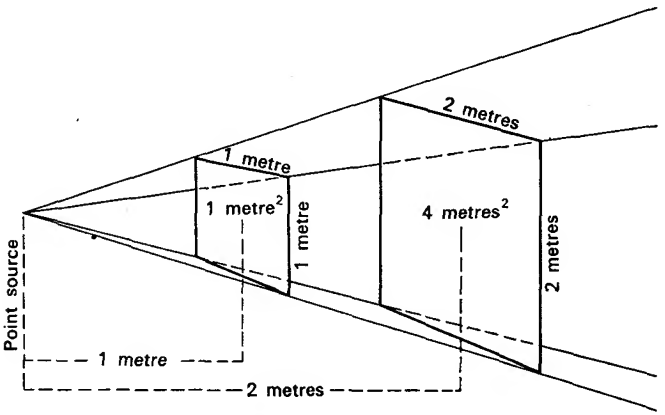


FIG. 9.4. Inverse square law.

Therefore the law may be stated in the following form:

The intensity of lllumination on a surface varies inversely as the square of the distance of such a surface from the light source.

The law is valid only for short distances when the source is very small or for greater distances when a large source is effectively a point. Expressed symbolically the law is $A \propto 1/d^2$, where A is the intensity of the illumination and d is the distance. Applying this formula to the example in Fig. 9.4 in the second position the area receives one-quarter the illumination of that of the first.

Although few of the illuminants in printing really conform to the requirements as point sources, many of them are employed at

sufficient distances for the law to be at least partially applicable. The most important of the illuminants in this context are the copyboard lamps of the process photographer and those used to expose the sensitive coatings on metal in all the graphic processes and to prepare screen process stencils. All practical workers in these fields are aware of the need to increase exposure times whenever it is necessary to increase illuminant distance.

Reflection. Light travels, if not impeded or diverted, in all directions from its origin, but for the present and many other purposes it is convenient to consider a single ray or beam.

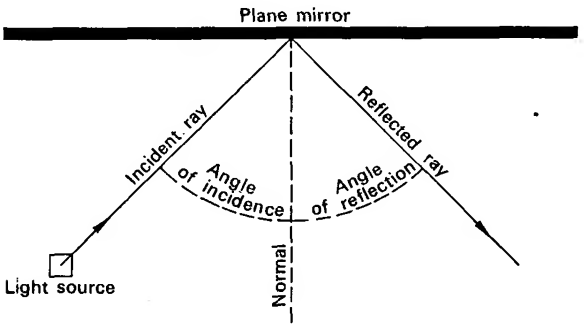


FIG. 9.5. Reflection by a plane mirror.

A ray emitted by some source will be reflected on reaching a plane mirror and it may be easily demonstrated that two laws of reflection are obeyed:

(a) The angle of incidence and the angle of reflection are equal both being referred to the normal, i.e. to the perpendicular to the reflecting surface.
(b) The incident ray, the reflected ray, and the normal lie in the same plane (Fig. 9.5).

With a mirror or highly polished metal surface the image is said to be specular: the image is reversed from left to right and, assuming a plane mirror, it appears to be of the same size and at the same

distance behind the mirror as is the object from the mirror face. Unlike some images produced through a lens system, mirror images cannot be projected: they are described as virtual.

All objects other than luminous bodies are perceived by the light they reflect, but since the majority of surfaces are more or less rough they cannot give a mirror image and the reflection is diffuse. Nevertheless, the laws of reflection remain valid; each of the small parts of such a surface are inclined at different angles and in many directions with the effect of scatter or random reflection (Fig. 9.6). It is necessary to observe that with all surfaces some absorption of light occurs. This is at a minimum in the case of a good mirror and at a maximum with a black surface although, even here, absorption will never be total.

FIG. 9.6. Diffuse reflection showing normals from an irregular surface (much enlarged).

The study of diffuse reflection is very important in assessing the printing qualities of paper. This subject is considered in Chapter 20.

To return to specular reflection. If a second mirror is placed suitably to receive the image from the first the second image will be laterally correct. This principle is applied to the periscope in which two inclined parallel mirrors permit an observer to see over an obstruction and to the most usual system of "direct lateral reversal" on darkroom process cameras. Negatives for photoengraving must give a laterally reversed image on the metal, and while in offset lithography there are normally more photographic stages, the image on the metal must be laterally correct or right-reading. For the former, three reflecting surfaces are needed while for offset two only are used, assuming in both cases that the aspect of the impression is to be that of the original.

Parallax. If two vertical pins are first viewed from a line joining them and then alternately from the left and right, there will appear to be a movement in the positions of the pins which may make it difficult or perhaps impossible to estimate their relationship, and thus error due to parallax may arise. This possibility of mistake is very important in the reading of instruments since the pointer is usually placed a little in front of its scale and consequently all readings must be made from directly in front (Fig. 9.7).

Parallax error is the cause, if scarcely the excuse, for the abuse often hurled at the football referee when he decides that the home

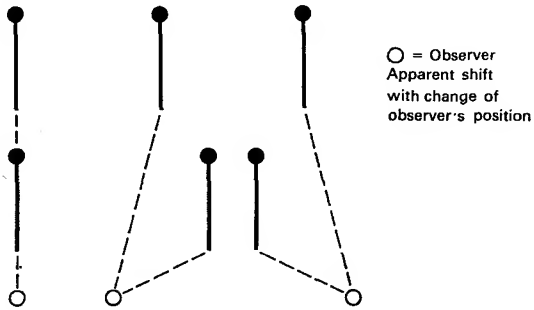


FIG. 9.7. Parallax error.

forward, with one opposing defender in view, is offside. In fact, it is almost impossible for a spectator, seeing the game from a position other than directly in line with the action, to judge the accuracy of an offside decision. Hence the linesman must not be stationary.

Transparent or otherwise. Materials are often classified for some of their optical properties into three types:

(a) *Transparent* in which the greater part of the incident light is transmitted without alteration as in the cases of water and glass.

(b) *Translucent* through which the light is largely or partially transmitted but which is scattered in the process, with the result that images are obscured or cannot be seen.

(c) *Opaque* materials transmit no light and most substances are placed in this class. It should, however, be noted that light on reaching the surface of an opaque material may be subject to specular or diffuse reflection and may be more or less absorbed.

Refraction. Light travelling obliquely from one transparent medium to another of different optical density is bent or refracted at the interface of the two media. The effect of refraction is easily observed when an object, partially submerged in water, is viewed from almost any position other than the vertical—the object appears to bend from the surface of the water downwards. Refraction occurs towards the normal (see the definition above) when the second medium is denser than the first and away from the normal when the second medium is the rarer.

Laws of refraction. (a) The incident ray, the refracted ray, and the normal at the point of incidence all lie in the same plane.

(b) The ratio of the sine of the angle of incidence to the sine of the angle of refraction is constant between the same media (for the trigonometrical ratios see Chapter 1). It should be observed that light incident at 90°, the normal, is not refracted.

Refractive index. The second definition above under (b) is Snell's law which may be set down symbolically as

$$\mu = \frac{\sin i}{\sin r},$$

where μ is the refractive index, i the angle of incidence, and r the angle of refraction.

It will be noted (Fig. 9.8) that the ray on emerging from glass to air is at the same, but displaced, angle as the incident ray.

Refractive index may be established experimentally by the use of the glass block as shown in Fig. 9.8; the information in Table 9.1 was obtained by carefully plotting various angles of incidence and the resulting angles of refraction. The average of the refractive indices is that of crown glass.

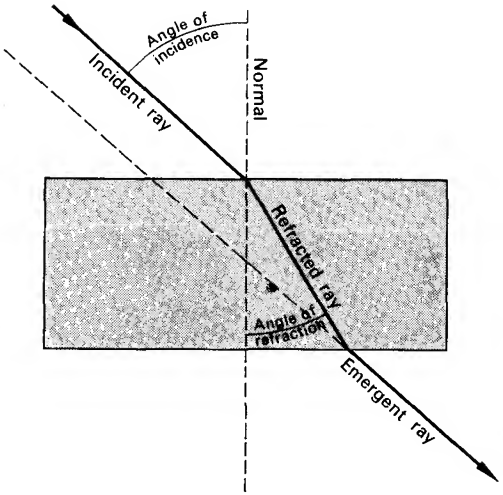


FIG. 9.8. Refraction by rectangular glass block.

TABLE 9.1

Angle of incidence i	Angle of refraction r	sine i	sine r	$\mu = \frac{\text{sine } i}{\text{sine } r}$
10·0°	6·5°	0·1736	0·1132	1·53
17·0°	11·0°	0·2924	0·1908	1·52
23·0°	14·5°	0·3907	0·2504	1·54
40·0°	25·0°	0·6428	0·4226	1·51
57·0°	33·5°	0·8387	0·5519	1·51

TABLE 9.2. REFRACTIVE INDICES OF SOME COMMON MATERIALS

Ice	1·31	Crown glass	1·52	Ethyl alcohol	1·39
Water	1·34	Flint glass	1·66	Benzene	1·49
Glycerin	1·47	Diamond	2·42	Carbon disulphide	1·63

Diamond, which is not so uncommon as is generally supposed, has a very high RI and this is responsible for some of its extraordinary qualities (see below).

The refractive indices shown above are those between air and the denser medium but, since the velocity of light in space differs little from that in air, the ratios from which the indices are derived represent closely the ratios of the velocities of light in space and in the second medium.

Critical angle and total internal reflection. As stated above, light is refracted away from the normal in passing into a less dense medium and consequently the angle of refraction is greater than the angle of incidence. If, as shown in Fig. 9.9, the angle of

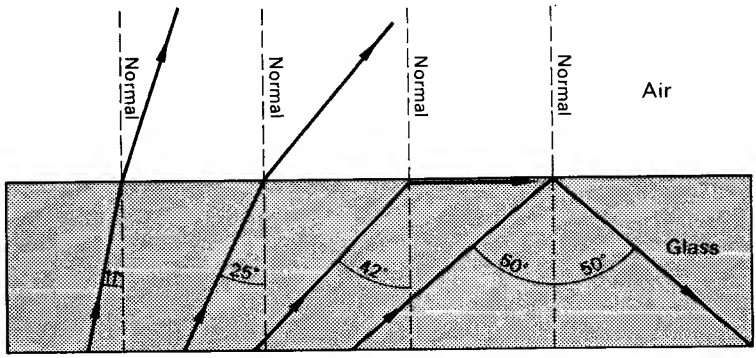


FIG. 9.9. Refraction from glass to air showing critical angle and total internal reflection.

incidence is increased, a value is eventually reached when the angle of refraction is 90° and the ray passes along the boundary between the media; any further increase will result in the light being turned back into the denser medium when the laws of reflection operate. The angle of incidence at which the first phenomenon occurs is the critical angle, while the second event is total internal reflection.

The higher the RI the lower the critical angle and, as a consequence, diamond becomes a blaze of light when the facets are suitably cut.

The critical angle of a given medium may be established experimentally and also, without great difficulty, mathematically. If, to simplify the formula, the grazing angle of 90° be taken as the path of the incident ray, then

$$\frac{\sin i}{\sin r} = \frac{\sin 90°}{\sin r} = \frac{1}{\sin r} = \mu \text{ (glass)}.$$

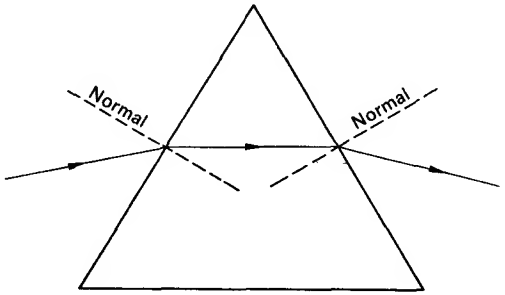


FIG. 9.10. Change of direction by a prism.

Taking the RI of glass as 1·5, the equation becomes $1/\sin r = 1 \cdot 5$ and thus $\sin r = 1/1 \cdot 5 = 0 \cdot 6666$ and, from tables, the critical angle is 41° 48′ usually set down as 42°.

The prism. As generally defined, a prism is a triangular solid figure of a transparent material, usually glass, with plane faces. Since the faces are not parallel, an emergent ray is given a direction different to that of the incident ray. In the equilateral triangle of Fig. 9.10 which may be accepted as one plane of a prism the incident ray is refracted towards the normal on entering the glass and away from the normal on emerging into air.

Total reflection of a right-angled prism. If parallel rays of light are received vertically on one of the right-angled faces of a right-angled

prism each ray will be reflected on reaching the hypotenuse where, since the ray within the glass is proceeding at an angle greater than the critical angle, it will be turned to emerge at the other right-angled face. In the action any image is laterally reversed, and thus the prism behaves in the same manner as a mirror.

The process gallery or free-standing camera is equipped, when intended for use in the photoengraving process, with a right-angled prism since the negatives must normally be prepared to provide prints on metal which are reversed from left to right. Although total internal reflection as shown in Fig. 9.11 is adequate for

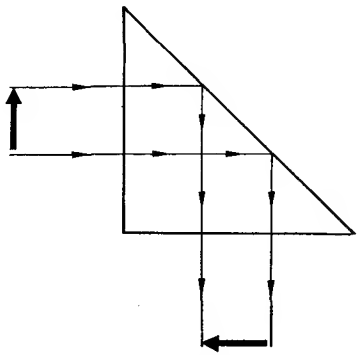


FIG. 9.11. Lateral reversal by right-angled prism.

most purposes, the hypotenuse is silvered to cope with the situation when the critical angle is not reached.

It is stated above that mirrors are usually employed in direct lateral reversal systems on darkroom cameras; mirrors have been used on the gallery cameras but prisms have been generally substituted since they are less liable to damage; in any case, these mirrors are not the familiar silvered glass but polished stainless steel, aluminium, or silver.

Dispersion by a prism. When white light is passed through a prism of the type shown in Fig. 9.10, on emerging it is seen to be

analysed into a band of colours if projected on a screen. This is the phenomenon of dispersion which is discussed in the next chapter.

Lenses. An optical lens is a transparent refracting medium, normally glass, bounded by two surfaces either or both of which are curved. The purpose of a lens is to cause light to converge or diverge after passing through it. Lenses are used to form enlarged

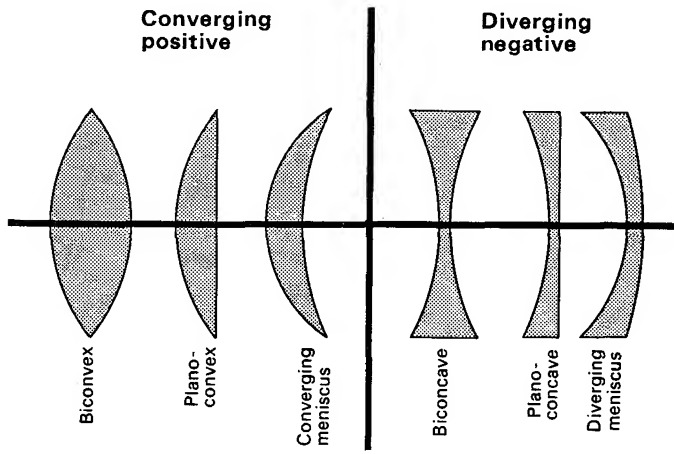


FIG. 9.12. Classification of single lenses.

or reduced images in microscopes, telescopes, cameras, and many other instruments; they are also used to correct defective vision.

Classification of single lenses. A single lens is made from one piece of the medium, usually glass. Compound lenses are built up of these simple components often using different types of glass.

Single lenses may be classified according to their structure and/or their optical properties; their faces are composed of any two of the three possibilities—convex, concave, and plane. Lenses in which the convex element is dominant are positive and converging; those predominantly concave are negative and diverging. (Fig. 9.12).

Refraction by lenses. A lens, however classified, may be considered as a means of bringing light travelling through it to a point; it may also be considered as a continuous series of small prism faces in which a ray incident normally at the centre is not refracted but in which rays passing through the lens elsewhere are subject to refraction. The angle of the hypothetical prisms increases outwards towards the margins in both positive and negative lenses but, since their aspects are opposed, the former converge the light while the latter diverge it.

Refraction of parallel light. In any lens system, light rays which are received from a source sufficiently distant are deemed to be parallel. In fact, for many of the lenses used in pure photography, infinity may not be much more than a few metres.

In Fig. 9.13 parallel rays are shown undergoing refraction and being brought to points on the optical axes of positive and negative lenses respectively. The points of convergence or divergence are the principal foci here designated F; the distances between F and the optical centres of the lenses are the focal lengths of the latter.

The focal point and the image produced by a negative lens are always on the same side as the object; the image is erect, i.e. of the vertical aspect of the object, virtual and diminished. The focal point of a positive lens is on the side opposite the object as is the image normally (but see the exception below). The image is usually inverted, real, and may be enlarged or reduced according to the capacity of the system.

Graphic construction of image by positive lens. In Fig. 9.14 the relation of object and image and the inverted aspect of the latter are shown geometrically; also shown are the principal optical symbols as far as the present purpose is concerned. F the principal focus (as already mentioned), f the focal length of the lens, u the distance of the object from the lens, and v the distance of the image from the lens.

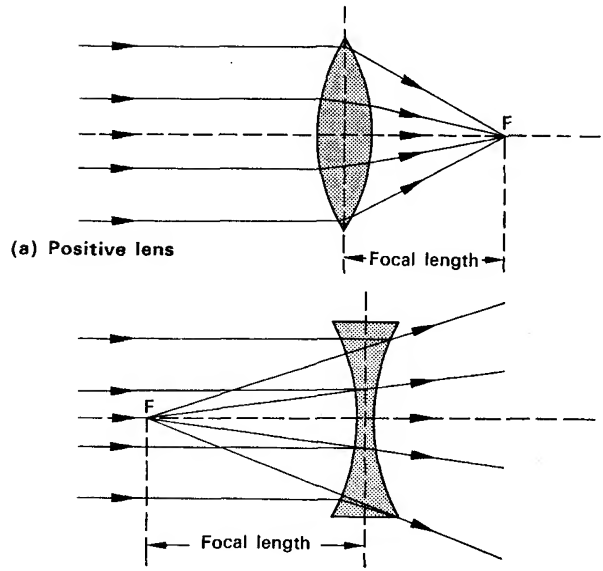


FIG. 9.13. Refraction of parallel light.

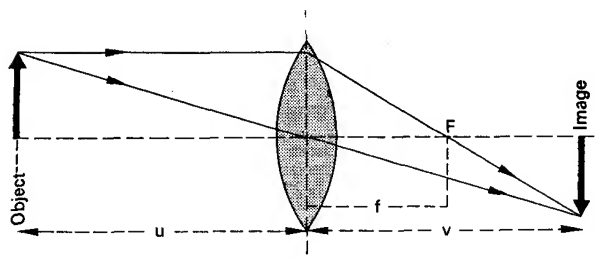


FIG. 9.14. Geometrical construction.

Formulae

The fundamental equation. It should be apparent from the above figure that a precise relationship exists between f, u and v; this is stated by the most important of the optical formulae:

$$\frac{1}{f} = \frac{1}{u} + \frac{1}{v}.$$

Given any two of these values the third may be calculated; thus to present a simple example:

If the object and image distances are respectively 20 cm and 10 cm, find the focal length of the lens.

$$\frac{1}{f} = \frac{1}{20} + \frac{1}{10}. \qquad \therefore \frac{1}{f} = \frac{3}{20}. \qquad f = \frac{20}{3}.$$

Focal length is 6·66 cm.

Magnification. This term has a general application; it stands for any degree of enlargement or reduction including same size. The symbol is M and this may be shown to be equal to the relation of the linear dimensions of the image to those of the object and thus $M = v/u$; it is possible to combine this with the fundamental equation and obtain two other valuable formulae:

$$v = f(1 + M) \quad \text{and} \quad u = f\left(1 + \frac{1}{M}\right).$$

Examples

(a) Given that $v = 40$ in. and $M = 1$ (same size) find f.
(b) Given that $u = 60$ cm and $f = 20$ cm, find M.

(a) $40 = f(1+M) = f\,2. \qquad \therefore f = \dfrac{40}{2} = 20$ in.

(b) $60 = 20\left(1+\dfrac{1}{M}\right) = 20 + \dfrac{20}{M}. \quad \therefore 40 = \dfrac{20}{M}. \quad M = \dfrac{20}{40} = \dfrac{1}{2}.$

In Fig. 9.14 it will be seen that $u = v$ and that therefore $M = 1$. Either of the formulae may be used to establish f:

$$v = f(1 + 1). \qquad \therefore v = 2f,$$

$$u = f\left(1 + \frac{1}{1}\right). \qquad \therefore u = 2f,$$

or the fundamental formula may be used:

$$\frac{1}{f} = \frac{1}{u} + \frac{1}{v}. \qquad \therefore \frac{1}{f} = \frac{2}{v}. \qquad f = \frac{v}{2} \quad \text{or} \quad v = 2f.$$

This result may be checked by measurement of the construction, but calculation is likely to be of greater accuracy.

Optical Instruments

The magnifying glass. This is a single biconvex lens and it typifies the exception referred to above. In order to function as expected, the object must be viewed from a distance of less than the

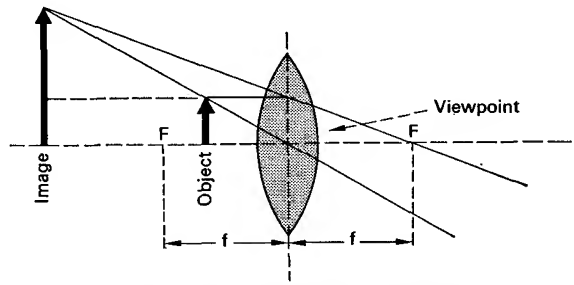


FIG. 9.15. The magnifying glass.

focal length of the lens with the result, as shown in Fig. 9.15, that the image is virtual, erect, and enlarged.

The hand magnifier is very familiar to workers in the graphic processes for the examination of halftone structures in negatives and positives, in metal printing, on proofs, and for the checking of register.

The microscope. This is among the rather large class of optical instruments which use a lens to produce a real image of an object

which is then viewed through a magnifying glass; the real image is given by the objective, the magnifier is the eyepiece (Fig. 9.16).

The enlarged image as viewed is strictly erect, but since it is derived from the original image it is actually inverted; to obtain

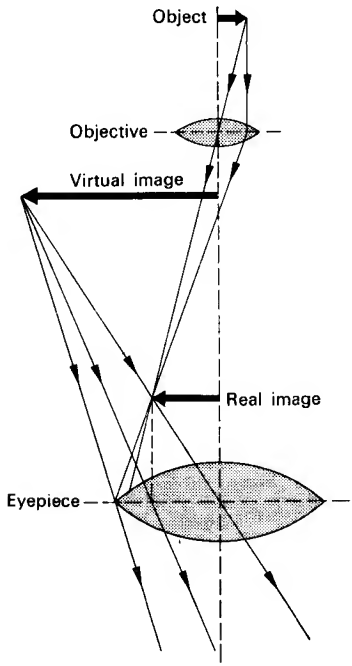


FIG. 9.16. A simple microscope.

an image with the attitude of the object a prism is inserted into the system. Binocular microscopes are used when it is necessary or desirable to examine surfaces with a low relief as, for example, with paper.

The camera. The pinhole apparatus has been considered above, but in view of the extremely long exposures which are needed it

has become little more than a curiosity, and the pinhole is replaced by a lens. The amount of light which reaches the sensitive emulsion is controlled by the lens aperture, this being usually marked in *f* numbers. The numbers state the relation of the diameter of the aperture to the focal length of the lens, and thus *f*/8 indicates an aperture which is one-eighth the focal length. Further, the numbers as usually encountered are arranged in such a manner that the square of a number is approximately twice the square of that next in the series. The word approximately is used because the system omits fractions which would be precise but which would also add an unnecessary complication. A part of the series is given with the squares which are not quite attained:

f/8 (square 64); *f*/11 (128); *f*/16 (256); *f*/22 (512); *f*/32 (1024).

All modern process lenses are marked with the diameter of the aperture in millimetres as well as by *f* numbers.

All photographic lenses tend to defects or aberrations, but since process lenses are normally used at relatively small apertures, most of these may be ignored; however, chromatic aberration cannot be overlooked in view of the importance of colour (this subject is considered in the following chapter).

Photocomposition. Phototypesetting, photosetting, filmsetting—the name appears to remain fluid—uses a complex optical system capable of enlarging or reducing the matrix characters as required; however, whatever the complexities, the principles of reflection and refraction as set down above remain valid, but detailed consideration of their application to this rapidly developing field is rather beyond the scope of this work.

The eye. The human eye, with its remarkable flexibility, must be the most wonderful of all optical instruments. The distance between the lens and the receptor mechanism being fixed, the curvature of the former is altered by the muscles to give the different focal lengths needed to obtain sharp images of objects variously placed. However, this muscular action may be defective and correction is often held to be necessary; if, for example the lens curve tends to be flat the error may be adjusted by a convex spectacle lens of greater curvature and thus shorter focal length or,

in the converse case, if the curve of the eye lens is too great a concave lens is used for correction. Astigmatism is that error which results when the muscles act unevenly, causing the eye lens to be curved more in one direction than another; this is corrected by a cylindrical lens placed with its axis at right-angles to the minimum curvature of the eye.

Diffraction. When a ray of light is directed through an aperture or across the edge of an opaque object, patterns of light and dark bands bordered by colours may be observed on a screen in suitable conditions. This phenomenon is diffraction and, while there are parallels, it must be considered as apart from refraction.

Process photographers are very familiar with the effect since a halftone screen in the camera back with the lens open always produces these patterns; they are also visible when street lights are viewed through a fog or through a slit.

Diffraction results from the wave character of light, the longer waves, i.e. the red, being bent more than the shorter blue radiation to produce these symmetrical and often beautiful interference patterns.

The formation of halftone. The ruled glass screen is used separated from the sensitive emulsion. When light is received on the surface of the screen it is reasonable to suppose that an umbra is formed under the opaque ruling and that this umbra will be fringed by a penumbra the extent and intensity of which is determined by the intensity of the light reflected by the given area of the original on the copyboard. Therefore when the photographic plate or film under the screen opening receives a full exposure from a white zone on the original a large area will be developable, but where the light emanates from a shadow a small area under the screen opening only will be exposed to result, on development, in a small opaque dot. (In practice the density of the dot is reinforced by a brief exposure to white paper or by a flash lamp.)

The above is a brief summary of the classic explanation of halftone formation—the penumbral hypothesis and in this manner the rendering of the various gradations of the original in terms of variously sized dots is accounted for.

However, while the hypothesis has the merit of some antiquity,

as far as the halftone process is concerned at least, it has been continually attacked in favour of diffraction. It is likely that the last word on this subject came from V. G. W. Harrison in 1952. It was shown mathematically in a manner outside the scope of this work that diffraction alone is sufficient to account for halftone formation.

Nevertheless, it is probable that all extant systems of halftone photography are based on the penumbral hypothesis. This may be ascribed to its simplicity since diffraction, if applied, would mean that every screen ruling must be regarded as needing its own set of screen equations.

The screen equation. It seems obvious that a mathematical balance must exist between the lens aperture, the extension of the camera (or the v of the optical formulae), the screen opening, and the screen distance. It is certainly surprising that most of the pioneer workers managed to get along very successfully without the blessings of optical science.

The balance or relationship suggested above is:

$$\frac{\text{Diameter of lens aperture}}{\text{Extension of camera}} = \frac{\text{Diameter of screen opening}}{\text{Screen distance}}.$$

While almost any numerical value may be assigned to this equation, practice has shown that the optimum value is one-sixtyfourth. Therefore, if the lens aperture is 10 mm, the extension is 640 mm, and given a screen of 4·8 lines/mm (120 lines/in.) the screen opening is 0·1 mm and the screen distance 6·4 mm.

The screen equation may be shown geometrically (Fig. 9.17).

The triangles ABE and CDE of Fig. 9.17 are similar since their corresponding angles are equal and therefore the corresponding parts are also equal, thus:

$$\frac{AB}{\text{Vertical from } E \text{ on } AB} = \frac{CD}{\text{Vertical from } E \text{ on } CD}.$$

The contact screen. This screen is used in intimate contact with the sensitive emulsion. It differs from the ruled glass screen in that the edges of the opaque structure are vignetted. The contact screen

therefore appears to have built-in umbra and penumbra and it may, in consequence, be held to support the penumbral hypothesis. Dot size in the negative or positive is controlled by exposure—the longer the exposure the greater the penetration by the light of

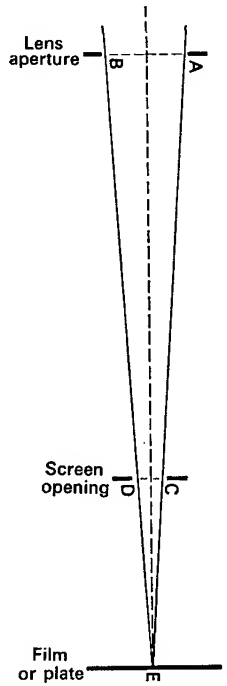


FIG. 9.17. Geometrical construction of screen equation.

the penumbral fringe or, in the case of exposure to an original, as the graduation approaches the highest lights the fully exposed areas become larger.

Densitometry. The most important aspect of a developed photographic emulsion in the technical sense is its density, and this implies its power of obstructing the passage of light. Density is measured

instrumentally and this is considered in Chapter 8 in the part devoted to electronics. It is proposed here to set down the forms under which density is assessed:

(a) *Transmission.* This is the relation of the light which passes through the emulsion to the light which is incident upon that emulsion, that is

$$\text{Transmission} = \frac{\text{Transmitted light}}{\text{Incident light}}.$$

Therefore given that the incident light is 100 units and that transmitted 10 units, the transmission is $\frac{10}{100}$ or $0 \cdot 1$.

(b) *Opacity.* This is the converse of transmission:

$$\text{Opacity} = \frac{\text{Incident light}}{\text{Transmitted light}}.$$

Therefore in the example in (a) the opacity is 10.

(c) *Density.* Opacity as expressed becomes cumbersome (see below) and as a consequence density is stated as the common logarithm of the opacity:

$$\text{Density} = \log 10 \frac{\text{Incident light}}{\text{Transmitted light}} = \log 10 \text{ opacity}.$$

The opacities 10, 100, and 1000 proceed by factors of 10, but the numbers are widely separated. The common logarithms of these quantities used to state density are 1, 2, and 3 respectively and, while they are clearly more convenient, they also express the relationship more precisely.

CHAPTER 10

Colour

INTRODUCTION

Coloured materials are everywhere; the normally sighted are able to distinguish hundreds or perhaps even thousands of different colours. It does, however, appear that colour discrimination is acquired since it becomes more refined with advancing civilization —primitive peoples are said to discern a dozen or so colours only, while women, as an additional burden, are stated to be more colour sensitive than men.

It may seem reasonable to hold that colour is wholly a property of the surface of coloured objects or of the substance of transparent coloured materials such as glass. However, there is no evidence of colour in very feeble lighting and there is certainly no colour in total darkness; further, many highly coloured surfaces viewed in the familiar mercury or sodium vapour street lighting become neutral greys.

There is, therefore, no doubt that colour must be in some manner largely a property of the type and intensity of the illuminant under which it is viewed.

The formation of bands or fringes of colour when sunlight passes through glass of certain geometrical shapes must have been observed from the very remote past, but it appears that the first seriously to study the matter was Sir Isaac Newton (1642–1727). A triangular prism was placed in the path of sunlight passing through a slit in an otherwise darkened room. The emerging radiation was received on a white screen and a ribbon of colours

ranging from a deep blue to a heavy red appeared. Since the admitted sunlight was white and the glass of the prism colourless, Newton concluded that the colours were components of white light and that the prism had analysed that light in some manner.

Newton stated that the colours he observed were seven—red, orange, yellow, green, blue, indigo, and violet—in accord, perhaps, with his views on a symmetrical universe, the seven planets, including the earth, of the ancient world, or the seven notes of the musical scale—the eighth being a return to the quality of the

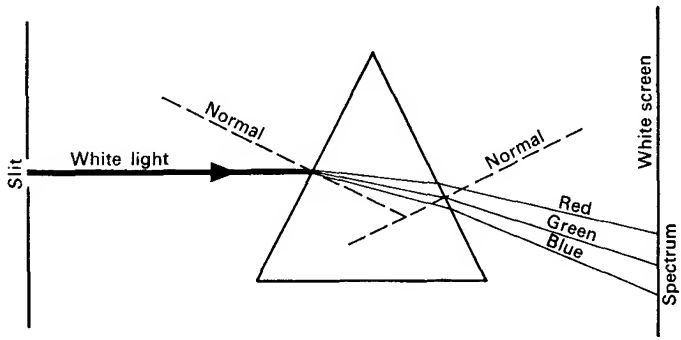


FIG. 10.1. Newton's experiment. Dispersion by prism. The experiment is improved by incorporating a simple lens projector in the system.

first—and so on. However, while many will claim to see more than seven, the dominant colours are three only—blue, green with a slightly yellowish tinge, and red (Fig. 10.1).

Since Newton's day it has become possible to study this ribbon of colour by means unknown at that time. The spectrum of white light has a wavelength range from 400 mμ to 700 mμ as discussed in the preceding chapter, and the differences in the observed colours are wholly due to differences in wavelength. Stating the wavelengths of the dominant colours only, blue occupies the range from 400 to 500 mμ, green the range 500–600 mμ, and red the range 600–700 mμ.

Mechanism of dispersion. Refraction is discussed in Chapter 9 and the refractive indices of various materials tabulated. Since refraction may be ascribed to the resistance afforded by a more or less transparent material to the passage of light when the light moves, other than normally, from one medium to another, it is reasonable to expect that the shorter waves will be more subject to the influence than the longer. This is, indeed, the case, and consequently radiation at the blue end of the spectrum is refracted more than the green which in turn is refracted more than the red.

While the refractive indices of the materials given in Chapter 9 may be deemed as those for white light, for many purposes they are strictly the indices for one narrow region of the spectrum.

Trichromatism. The manner in which the eye receives colour is very complex. Briefly, it is generally accepted that the sensitive area opposite the lens of the eye has a series of extremely small projections divided into two groups; the rods which function in light of low power and which have no special response to colour, and the cones which are the colour receivers; the latter are individually sensitive to either blue, green, or red, and these, it should be noted, are the dominant colours of the spectrum. Consequently all colours are seen as mixtures of two or more of these primaries—this may be established experimentally and any colour may be matched by carefully adjusted quantities of each light. The spectral colours are rare in nature outside the rainbow.

Colour deficiency. While colour discrimination is acquired and thus variable in normal-sighted persons, it is stated that about 8 per cent of males and a very much lower proportion of females suffer from defects in colour sensitivity. These defects are generally partial but, in a very small number of cases, some are total. 'Colour deficiency' has been substituted for the once common and inaccurate 'colour blindness'; the effect is that certain colours are seen as greys by most sufferers and, for the extreme cases, everything is observed in terms of a grey scale. It is to be remarked that few or none are normally aware of the trouble since it is impossible for a fully sighted person to convey his experience of the missing colours.

Accurate colour vision is important in almost all sections of the

printing industry, and in many branches it is imperative. Those wishing to train as process colour photographers, colour fine etchers, colour retouchers in photogravure and photolithography, machine operatives likely to be engaged in colour printing by any method, lithographic artists, and certain types of process artists should all be subjected to prior tests, the most usual of which is that perfected by the Japanese Ishihara. Many individual employers and most associations are indeed already insisting on tests for colour efficiency.

Selective absorption. A mirror reflects almost the whole of the incident light and, although its reflecting surface is apparently colourless, every colour is reflected unchanged. A white material such as semi-matt pure white paper diffusely reflects also the incident light quite well.

However, given that white light, ideally sunlight, is composed of a number of colours—predominantly blue, green and red—a surface is coloured because some part or parts of the incident light is destroyed by absorption and the rest reflected by that surface. This happening is known as selective absorption and thus a material is a spectral red because the blue and green elements of the light are absorbed.

Trichromatism applied. It has been said that while the evidence supporting the idea of trichromatism is largely derived from the study of the mechanism of vision it is also confirmed by the striking success of its practical applications. The famous experiment before the Royal Institution in 1861 made by the great physicist Clerk Maxwell (1831–79) was the first really successful and certainly dramatic demonstration of a three-colour process. Maxwell prepared three-colour separation negatives—using blue, green, and red filters—of a tartan ribbon. From these negatives, positives were made and projected simultaneously and in register on a screen through the colour-separating filters. While today the inefficiency of his photographic materials is well known, Maxwell's achievement remains a triumph—indeed the experiment has been repeated successfully. It may be said that all colour photography is derived from this beginning. Eight years after Maxwell's demonstration a book written by the Frenchman Louis Ducos du Hauron

proposed probably every application of the principle to printing, thus anticipating some of the actual developments by from 25 to 40 years.

Additive processes. The use of colour-separated elements projected by means of white light through the separating filters is the basic application of additive trichromatism. Additive in this context means the addition of coloured lights in the manner associated with Clerk Maxwell and the experiment discussed above. All the earlier processes of colour photography were additive, and while projection persisted and obviously contributed much to the beginnings of colour cinematography, single-plate processes in which blue, green and red elements as mosaics were provided as transparencies, to be viewed by transmitted light, were of substantially greater importance both for their own merits and for their part in the development of colour in pure and applied photography. Lumière autochrome, which used dyed starch grains, was perhaps the most successful; other processes employed various geometrical structures, some very close to halftone.

Subtractive processes. As has been stated, the earlier processes may be considered as the addition of coloured lights whether seen as projected or viewed by transmitted light. It is clear, however, that such methods cannot be successful when the colour images are to be examined by reflection as in printing or as dyed pictures on paper. (It is unfortunate that "printing" is used for both mechanical impression and in pure photography.) For example, the simultaneous projection of blue, green, and red lights gives a near white according to the accuracy of the colours, while if superimposed on paper the effect would be black or nearly so; any two of the colours together would result merely in some brown or neutral tint since each would, in principle, absorb two-thirds of the spectrum.

Therefore some application of selective absorption as defined above must be adopted.

The word "primary" has been used earlier to denote the three dominant spectral colours, but artists have long employed this word for very different colours even though two of the names are the same—these so-called primaries are yellow, blue, and red.

It is easily demonstrated that yellow is actually a secondary colour since it may be compounded by the superimposition of spectral red and spectral green lights; therefore when a yellow pigment on paper is viewed in white light, red and green are reflected and blue absorbed or, in other words, yellow is what it is by the subtraction of the blue component of white light (Fig. 10.2).

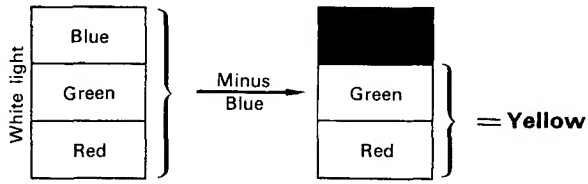


FIG. 10.2. Yellow by subtraction.

Similarly, the remaining primaries of the artist are each built up of two reflected components of white light while the third is subtracted (Fig. 10·3).

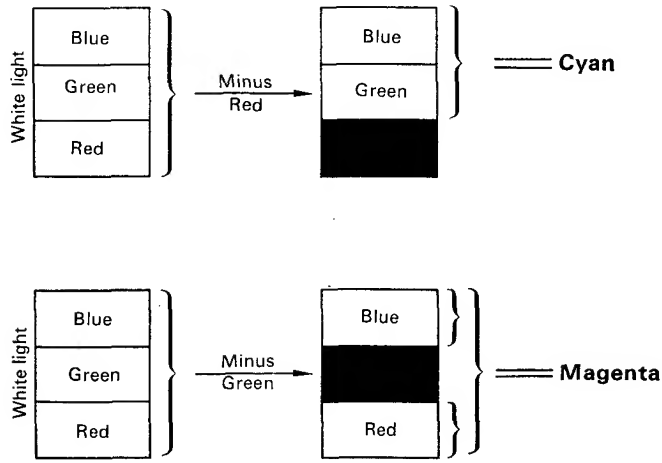


FIG. 10.3. Cyan and magenta by subtraction.

Accordingly all reflected colours, and few colours are seen by transmission, owe their characters to a greater or lesser absorption of one, two, or three of the additive primaries.

It will thus be observed that in an ideal subtractive three-colour system all the colours of nature are possible—even the spectral primaries as shown below—and that the colours will be sufficiently luminous to be acceptable; the latter being impossible by reflection use of the additive colours.

Colour television is one of the few modern applications of the additive principle, and it functions successfully because the blue, green, and red elements of the cathode ray tube are viewed as transmitted light.

Colour printing, other than the older techniques such as chromolithography drawn to stone or plate, is almost wholly an application of the subtractive principle in some manner or other. It is also basically trichromatic even when a fourth grey or black is used as is commonly the case in letterpress and offset lithography and perhaps rather more rarely in gravure. The use of two further colours, usually as reinforcements for the cyan and magenta, sometimes the practice in offset-lithography cannot be deemed as a departure from the trichromatic principle.

The defects of the three-colour process. If the ideal colour separation process were available, if the three-colour inks were perfect and if the actual printing methods were capable of being rigidly controlled, the three-colour process would be all but mechanical: this it certainly is not.

Many workers believe that the first of the faults are the filters used for the separation of the colours. In fact the filters, while departing a little from the probably unattainable ideal, are reasonably accurate (Fig. 10.4).

It should be noted that the differences in the filters are not in colour quality but in the actual transmissions. These differences are adjusted by changes in the exposure times on the camera to compensate for the varied quantities of light passed.

The panchromatic, or full-colour-sensitive, plates or films used are imperfect in so far as no emulsion at present available is equally sensitive over the whole spectrum. This weakness, however, is

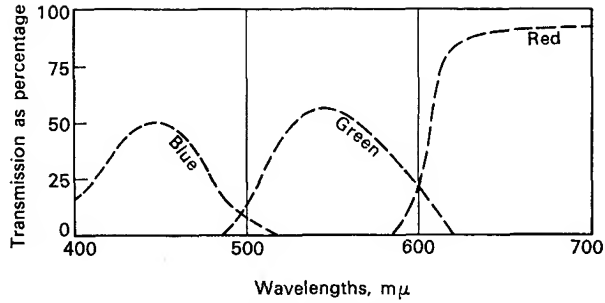


FIG. 10.4. Approximate transmission curves of typical trichromatic filters.

adequately corrected in the same manner as for the filters by giving more or less exposure according to the data supplied by the manufacturers with each batch of plates and films.

By far the greatest of the defects of the process are those of the inaccuracies of the inks, more particularly of the cyan and magenta. It has so far been found impossible to use pigments that are sufficiently stable to light and to time and that otherwise conform to the rather stringent demands of the industry (Fig. 10.5).

The actual weight of ink and impression are generally controlled by the machine operator and the variations possible—and even

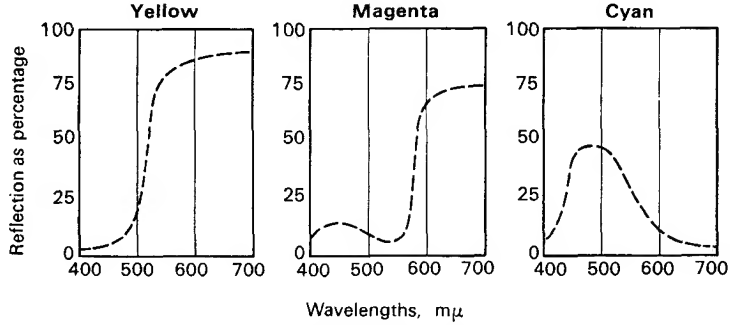


FIG. 10.5. Approximate reflection curves of standard trichromatic inks.

probable—in both, contribute something to the defects of a more fundamental nature discussed above. However, the printing machine is being improved towards spectrometric controls of colour density (see below) and towards precise and uniform impression.

Correction of colour defects. While the methods of colour correction in the graphic processes are beyond the scope of this book, one example to illustrate a complex subject will be of value. Inspection of Fig. 10.5 will indicate that while the yellow ink is quite close to theoretical requirements, the cyan ink is very far removed from those requirements. The cyan absorbs more than 50 per cent of the blue it should reflect. Blue absorption is a function of yellow; indeed, it defines yellow, and therefore the cyan ink acts as if it has a yellow component. Since it is manifestly impossible to do anything about this failure of the cyan directly, that region of the yellow printing plate which carries the unwanted yellow of the cyan must be reduced or even removed completely—and this in spite of the reasonable adequacy of the yellow ink. The same type of error exists in the magenta ink demanding similar correction. Colour correction is achieved in many ways: by photographic masking, by the manual methods of fine etching in photoengraving, by the analogous dot reduction of photolithography, and by the techniques of retouching the continuous tone negatives and positives in the photogravure process.

Further, partially or considerably colour corrected negatives, positives, and directly engraved plates may be produced by applications of electronics (see Chapter 8).

The lens and colour photography. The single lens, i.e. one with a single component only, must suffer from several errors or aberrations. The most important in the present context is chromatic aberration. In the matter above on dispersion it is stated that refraction is greater for the shorter wavelengths of blue than for the red, and in consequence the focal point for each of the colours is different, or to set down the actual effect, with a single lens it is impossible for the colours to be in focus in the same plane. A lens suffering from chromatic aberration would be quite unsuitable for colour separation in any graphic reproduction process. Lens

designers are able to employ the various refractive indices of different optical glasses to achieve substantial correction of the aberration (Fig. 10.6).

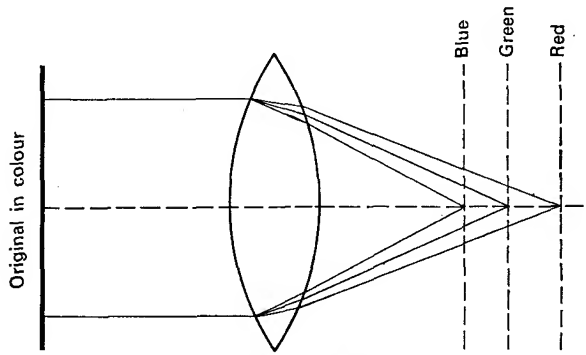


FIG. 10.6. Chromatic aberration of single lens.

TABLE 10.1. REFRACTIVE INDICES OF TWO OPTICAL GLASSES

Blue	Green	Red	
1·640	1·624	1·620	Dense flint
1·517	1·510	1·506	Light crown

400 500 600 700

Wavelengths in mμ.

Correction for two colours in the achromatic lens is adequate for the simpler forms of colour photography, but for process photography and advanced technical work much greater correction is necessary. This is achieved in the apochromat which, with its several components, practically attains coincidence of the blue, green, and red separated images (Fig. 10.7).

The eight colours of the three-colour process. Given that each of the three colours of an ideal subtractive process absorb one-third of the spectrum of white light, it is possible to show that eight colours, including white and black, are immediately available. (See *Frontispiece.*)

Mixtures of these eight elements in various proportions give in principle a very wide range of other colours. In practice, however, the inadequacy of the inks, particularly of the cyan and magenta, prevents the complete realization of the ideal. On account of the unwanted absorption of blue by the cyan and magenta, what

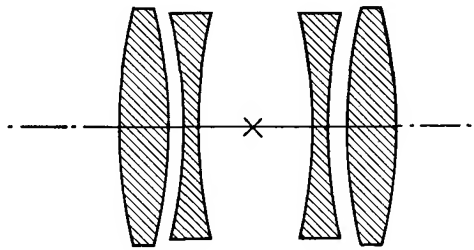


FIG. 10.7. A typical apochromatic process lens (courtesy of Wray (Optical Works) Ltd.).

should be black tends to be a rather grubby brown—this is, of course, one of the reasons for the fourth printer—while the paper may not be as white as expected.

Further, any subtractive process is subject to surface reflection particularly when high gloss inks are used; this addition to the system tends to dilute or partially desaturate all the colours.

Terminology of colour. As well as the standard names for the trichromatic inks which are slowly being accepted, even in the printing industry, certain terms for other aspects of colour are employed by specialists:

Hue. The kind of colour—yellow, red, cyan, etc.

Saturation. The purity of the hue—the colour under examination departs from saturation as it is adulterated with white or greys.

Luminance. The degree of the incident light reflected or transmitted by the colour in question. Brightness is an alternative word.

Measurement and specification of colour. There is a growing need for some means for the expression of colour in precise numerical terms. All the earlier systems depended on colour matching and reference to a code usually consisting of numerals and letters. The best known of these are:

(a) *Ostwald,* advanced by the eminent German chemist F. W. Ostwald (1853–1932) in which the full colours are numbered and the desaturation (see above) indicated by letters.

(b) *Munsell.* This system was devised by an American art teacher A. H. Munsell (1858–1918). It bears some resemblance to the former but it is capable of much greater precision. Solid colour patches are referred to nine neutral steps from white to black to determine degree of desaturation.

Both the Ostwald and the Munsell systems depend upon the colour discrimination of a viewer and therefore instrumental means to determine and express colour are desirable for many purposes.

(c) *CIE.* These initials indicate Commission Internationale d'Éclairage (International Commission on Illumination). This system was first stated in 1931 and it has been modified from time to time since. Any colour is expressed in terms of quantities of precisely specified blue, green, and red examined under precisely specified illuminants.

The quantities of each component are stated as fractions of unity and, since the three sum to one, two quantities only define a colour.

Instrumental determination of colour. It is apparent that numerical statements of colour values are obtainable only by the use of instruments. Consideration of the spectrophotometer and the colorimeter appears under electronics in Chapter 8.

Standard trichromatic inks. The British Standards Institution has published over the years several specifications for three- and four-

colour inks. The need for revision has arisen as improvements become possible.

The most recent is BS 4160: 1967 which deals with letterpress inks for three- and four-colour printing. Rather surprisingly, perhaps, in view of the remarkable progress of offset lithography, the only specification of inks for that process is BS 2650; 1955, and this is generally held to be obsolete; in fact, the makers of offset litho inks tend to accept the standard for letterpress inks, BS 3020: 1959 and the BS 4160: 1967.

There appears to be no standard specification for trichromatic intaglio inks.

The components of a subtractive colour system. Although trichromatism remains the basis of any additive or subtractive system, the proposition, due to Dr. H. E. J. Neugebauer, is advanced that eight components are actually available in the latter since the principle of selective absorption must be accepted.

Given solids which are superimposed in 4, 5, 6, and 7, the components are:

(1) *Yellow* (= minus blue).
(2) *Magenta* (= minus green).
(3) *Cyan* (= minus red).
(4) *Red* (yellow plus magenta = minus blue, minus green).
(5) *Green* (yellow plus cyan = minus blue, minus red).
(6) *Blue* (magenta plus cyan = minus green, minus red).
(7) *Black* (near) (yellow plus magenta plus cyan = minus blue, minus green, minus red).
(8) *White* (the paper).

While the printing application is set down above, the proposition may be assumed to have reference to any subtractive trichromatic process. (See *Frontispiece.*)

Part III

Chemistry

CHAPTER 11

Chemistry: Inorganic and General

Introduction. Although chemistry, as one of the most important of the physical sciences, appears to belong so aptly to the world of today, it, or perhaps more properly its antecedents, reach back to the ancient Mediterranean civilizations.

It is said that the word is derived from an early name for Egypt and that 'chemistry' means, accordingly, the 'Egyptian Art'. While this art seems very remote from the science of the present, it was largely concerned with very many practices which have a bearing on modern technology; the extraction of metals from their ores, the making of glass, drugs, dyeing, and the control of fermentation to produce wines and beers.

However, with the passage of time a major activity of those who became known as "alchemists" was the search for a means to convert base metals into gold; this search proceeded for almost 2000 years and the alchemists were regarded as magicians as, indeed, they might well have been had the quest succeeded.

The alchemists have frequently been ridiculed, but their principal object, "the transmutation of metals", is at last accepted as within the bounds of possibility, and it may one day be achieved. Nevertheless, there is no doubt that very much of their work, futile as it has seemed to many of the successors of the alchemists, laid the foundations for a good deal of present-day chemical principles and practice.

Divisions of chemistry. The science may be very broadly defined as the study of the composition of substances, the resolution of substances into simpler forms, and the formulation of the laws governing the observed changes.

Chemistry is divided for convenience into several sections, the most important being:

(a) *Inorganic chemistry*, which is that part of the science concerned with the elements and their compounds (see later) with the exception stated below. This branch is also devoted to the more refined theoretical aspects of the subject under the heading of "theoretical chemistry".

(b) *Organic chemistry* was originally supposed to be the science of the materials derived from or produced by living beings. The present definition is: *the chemistry of the compounds of carbon excluding the carbonates and to some extent the oxides of that element.* This modern definition does not make the original invalid since substances derived from animal and vegetable life are also carbon compounds. As a consequence of the almost unique properties of carbon, the number of known organic compounds is of the order of a half million while the number of possible compounds seems to be illimitable. It is likely that almost all inorganic compounds are known or envisaged, and it appears that the total is about 50,000.

(c) *Physical chemistry* impinges to a considerable extent on physics. It is concerned with the impact or influence of forces upon chemical reactions and with the study of the conditions in which chemical processes attain maximum efficiency. This latter is of very great importance in industrial techniques and in chemical engineering.

Physical and chemical changes. Water exists in three states—as ice, as liquid, and as gas. The transition from one state to another is easily effected, and any change is reversible while, apparently, the actual composition of the substance remains unaltered.

Wood and coal may be burned and the products of the combustion are flame, smoke, and ashes. This action, unlike the above,

appears to be irreversible, and the original materials have been converted to quite distinct and perhaps simpler substances. The flame must be excluded since it is mainly evidence of the rapidity of the process.

The first is an example of a physical change which is defined as a change of state or condition. Further examples of physical changes are: changes in temperature, in barometric pressure, in atmospheric humidity, in the direction of light by reflection and refraction, and the many other changes of state between solid, liquid, and gas.

The second is a chemical change, and it is obvious that a change of substance is involved. A great part of chemistry is concerned with this type of change; many examples appear below.

The elements. That matter as commonly observed is composed of simpler substances is a view that has long been held. Following the speculations of many of the Greek philosophers it was believed that all matter is composed of four elements and that the wide differences between one substance and another were due to the varying proportions of these elements. Fire, air, water, and earth were separately indivisible—they are elements because they are unique and pure. It is of great historical interest that the idea of fire as an element persisted in essence to the early years of the last century among the more traditionally minded. It was supposed that "phlogiston" was present as a component in all combustible materials and that it was liberated during burning, while the incombustible residue was a "calx". Clearly if a component is lost, the total weight of all the products of combustion would be less than that of the original material. However, the development of experimental chemistry continued and it was shown that combustion is combination with oxygen and that, consequently, the products are heavier than the unburned original.

More and more metals and gases were isolated as discoveries multiplied and many appeared pure in the sense that attempts at division into simpler substances were unsuccessful. Therefore the ancient view that an element is pure and unique was maintained although the classic elements were discarded.

An element is defined as a substance which cannot be separated

by any chemical process into simpler substances. It is necessary to include in the definition the reservation restricting it to chemical terms since in the light of present knowledge of atomic structure some form of division is possible.

The earliest serious attempt at an ordered classification of the elements was made by the great French chemist A. L. Lavoisier (1743–94). He arranged the then known elements, about thirty in number, in four sections according to their chemical character; metals were regarded as quite distinct from non-metals—a distinction still of practical importance although not of the chemical significance previously supposed.

Later, as knowledge advanced and the number of known elements increased, the tentative attempts of many investigators culminated in the definitive periodic table of the Russian D. I. Mendeléeff (1834–1907). This table, based at the time principally on atomic weights (see below), is considered one of the greatest achievements in the history of the science.

The atom. Given that an element, as defined, is a unique substance, it follows that, assuming the possibility of subdivision, the ultimate particle of that element must be postulated. This view was advanced by many Greek philosophers and attacked by as many others; the latter held that matter is continuous and therefore infinite subdivision is possible in principle.

Neither view was capable of experimental proof at the time; indeed, it was commonly supposed that all problems were soluble by pure thought alone, and the idea of the necessity of experimental verification arose much later in the perhaps more prosaic minds of Arab doctors, while with the scientific advances of the sixteenth century onwards it became increasingly evident that matter is indeed composed of extremely small particles. Sir Isaac Newton (1642–1727) supposed that the differences in the character of different substances are due to the variations in density and size of their particles.

It is, however, John Dalton (1766–1844) who must be given a very great part of the credit for the restatement of the rather tenuous classical hypothesis on the structure of matter. Dalton published his theory—theory because all of his proposals were

supported by experimental evidence or by rational deductions from that evidence—in 1808.

Further, the whole of Dalton's statements remain valid in all respects other than the reservations due to the discoveries of modern physics on the structure of the atom itself.

Dalton's statements may be paraphrased as under:

(a) All matter is composed of extremely small particles (or atoms).

(b) The chemical processes of analysis and synthesis involve the separation of atoms from atoms and the union of atoms to atoms respectively. This implies the indestructibility of the atom in the chemical sense.

(c) Each element has its own distinctive type of atom. This statement is fundamental to the definition of an element since, if the elements are unique, their ultimate particles must also be unique.

Atomic weights. Dalton's work involves the proposal that the atoms must be differentiated in density and volume from element to element—a view tentatively advanced much earlier, indeed, by Newton.

It became apparent, therefore, that it was necessary to determine the weight relationship of the atoms of the different elements if the science was to move forward. For many reasons, beyond the scope of the present work, the actual weight is less important than the relative weight.

Having established that the lightest gas is hydrogen and given that the hydrogen atom is of unit weight, all the other atoms were referred to that atom and the system of atomic weights founded. However, the atomic weight assigned to oxygen (O = 16) has long been the standard, but this is being replaced by that of carbon (C = 12); the former is used in this work.

The atomic weight of oxygen is 16 and that of aluminium is 27. This is to state that the weights of the atoms of these elements are effectively sixteen and twenty-seven times the weight of the atom of hydrogen respectively.

(A more complete table giving atomic weights and other information is given on pp. 240–3.)

Chemical symbols. All chemical action involves the separation and union or combination of atoms, and, in order to shorten the labour of written discussion, Dalton invented a series of geometrical symbols to indicate the atoms of the different elements. While these were admirable in their time, the continuing discovery of elements made further development of the scheme difficult if not impossible. J. J. Berzelius (1779–1849) suggested the basis of the now universally accepted system. The initial letter, or the initial and one other letter, is taken from the name of the element. Since the words for the common elements often vary from language to language, the Latin version is often selected to derive the symbol. Thus Au from *aurum* stands for gold; Fe from *ferrum* is the symbol for iron; and Pb from *plumbum* means lead. This minor difficulty is hardly of consequence with the majority of elements since they were unknown to Caesar and their names are as recent as their discovery. However, the classic form is usual: O stands for oxygen; H is hydrogen; and N is the symbol for nitrogen. The symbols for the common alkali metals are rather curious in origin. Again, they were also not known to the Romans but Latin versions of Arabic words which have a somewhat vague or dubious reference to these elements are used: Na from *natrium* and K from *kalium* stand for sodium and potassium respectively. These familiar names themselves are also in a Latin form.

Many of the symbols and names of the newer elements suggest the connection with the country or even the continent of the discoverer; among them Re from rhenium, the Rhine. The origins of Ge, germanium, and Eu, europium, are obvious.

While the symbols are often said to indicate the elements, strictly they stand for the atoms of the given elements. (A list of the symbols appears in the appendix tables, pp. 240–3.

Molecules. A molecule is defined as the intimate chemical union of two or more atoms; the atoms may be of the same or of different elements. Further, a molecule is the smallest particle of a substance able to exist independently with very few exceptions, usually of brief duration.

The elementary gases—hydrogen, chlorine, nitrogen, etc.—are diatomic, i.e. the normal form of their smallest particle is composed

of two atoms almost rigidly bonded to form one molecule. Thus the molecules of these gases are represented symbolically as H_2, Cl_2, N_2, the number being a factor.

Compounds. A compound is a substance composed of two or more elements in chemical union in which the components usually appear to have lost their identity and in which separation of the components is often difficult and sometimes extremely so.

Since, as stated above, the molecule is, with the reservation noted, the smallest particle of matter, it is implicit that the unit of the combination is the molecule. Thus sodium chloride or common salt is, as the chemical name indicates, a compound consisting of the alkali metal sodium and the noxious gas chlorine. Water is a compound of hydrogen and oxygen. It is to be noted that in both cases the compounds appear to have no resemblance to their component elements and that separation or decomposition is very difficult in the first case and difficult in the second. Electrolysis is employed commercially to obtain sodium and chlorine from common salt, while the same method and several alternatives are effective with water.

The molecules of these compounds are represented by the formulae NaCl and H_2O respectively; these indicate that one atom of sodium and one atom of chlorine are combined to form one molecule of sodium chloride, and that two atoms of hydrogen are combined with one atom of oxygen to form one molecule of water.

Since the component atoms have a definite atomic weight, the proportion of each in the molecule and consequently in the compound is constant. In the above examples, given that the atomic weights of sodium, chlorine, hydrogen, and oxygen are 23·0, 35·5, 1, and 16, sodium chloride consists of 23 parts by weight of sodium and 35·5 parts of chlorine, while water consists of 2 parts (2×1) of hydrogen and 16 parts of oxygen also by weight.

Mixtures. In the compound ferrous sulphide with the formula FeS, reference to the tables indicates that the AW are 55·8 and 32·0 respectively; therefore in the molecule and consequently in the compound, 55·8 parts of iron by weight are combined with 32·0 parts of sulphur, also by weight.

Given the difficult task of weighing accurately 55·8 g of iron filings and 32·0 g of powdered sulphur, these substances may be added together and carefully agitated to form a uniform mass which would contain the elements in precisely the same proportions as are present in the compound.

However, there is a clear distinction: in the compound the iron and sulphur have lost their identities and separation into these components is only possible with considerable difficulty. In the second case the elements are obviously unchanged and separation is achieved very easily; the iron may be removed by the use of a magnet, the sulphur may be separated by a sieve with a mesh smaller than the filings or by a solvent from which it may be recovered by evaporation.

The second case is an example of a mixture, and many others of the type may be cited; copper turnings and crushed carbon, common salt and sand, aluminium powder and sugar, or even flour and currants.

A mixture is defined as a mechanical intermingling of any number of different substances which may be separated by suitable physical means and in which the constituents may be in any proportion. The last is the fundamental distinction which differentiates compound and mixture; in the former the components must be in an exact ratio by definition while in a mixture they may be in any quantity.

Molecular weight. The conception of molecular weight arises naturally from the matter of the above. Since molecules consist of atoms in simple numbers, by definition a fraction of an atom is impossible, and since all atoms have a definite weight relationship with the atom of hydrogen it follows that the relative weight of any molecule may also be expressed in terms of the hydrogen atom. At this point it should be observed that the relative weights of atom and molecule are usually prefixed by the initials AW and MW respectively—one further example of the satisfaction of the need for a concise symbolism. Some examples are given to illustrate the derivation of MW when the molecular formulae and the AW of the component atoms are known (Table 11.1).

Formulae and equations. The science of chemistry is largely

TABLE 11.1

Substance	AW	AW	Formula	MW
Hydrogen chloride	H = 1	Cl = 35·5	HCl	36·5
Sodium bromide	Na = 23	Br = 80	NaBr	103
Ferric chloride	Fe = 56	Cl = 35·5	$FeCl_3$	162·5
Calcium iodide	Ca = 40	I = 127	CaI_2	294
Carbon dioxide	C = 12	O = 16	CO_2	44

concerned with the study of the formation of compounds from their elements or from simpler compounds, i.e. the process of synthesis, and the converse, the separation of compounds into their elements or into simpler compounds, i.e. the process of analysis.

The use of symbols to indicate the atoms of the elements has been briefly discussed. Formulae have also been mentioned; a formula is defined as a means of representing a molecule in terms of its component atoms using the accepted symbols for the purpose. Where a molecule contains or consists of more than one atom of the same element, this is indicated by a number at the lower right edge of the atomic symbol. (Examples are given in Table 11.1.)

Chemical changes—the processes of synthesis and analysis, reactions such as those between acids and metals—are also completely represented by the atomic symbols, the molecular formulae, the mathematical symbol + with the meaning "added to and reacts with" and = meaning "results in and gives an equal weight of".

Thus when hydrogen is ignited in air it reacts with the oxygen present in the manner shown symbolically:

$$2H_2 + O_2 = 2H_2O$$

This equation must show equal total atomic or molecular weights to the left and to the right.

The equation interpreted states: 2 molecules of hydrogen each of MW 2 react with 1 molecule of oxygen of MW 32 to result in 2 molecules of water each of MW 18. The sum of the MW on each side of the equation is 36.

It will be seen that the number which appears at the left-hand side of the molecule, as in $2H_2$ and $2H_2O$, acts as a factor or coefficient.

In suitable conditions hydrogen will combine directly with chlorine to form hydrogen chloride or hydrochloric acid:

$$H_2 + Cl_2 = 2HCl$$

That is, 1 molecule of hydrogen reacts with 1 molecule of chlorine to result in 2 molecules of hydrogen chloride. The sums of the MW on each side of the equation are clearly equal.

Further examples of equations are given below under "acids, bases, and salts".

Valency. Valency is defined as a numerical value which indicates the combining power of an atom. This combining power is referred directly or indirectly to that of the hydrogen atom which has a valency of 1. Valency may usually be deduced by inspection of the molecular formulae (Table 11.2).

TABLE 11.2

HCl	1 atom of hydrogen is combined with 1 atom of chlorine
HBr	1 atom of hydrogen is combined with 1 atom of bromine
HI	1 atom of hydrogen is combined with 1 atom of iodine

Since hydrogen is given as monovalent (of valency = 1), chlorine, bromine, and iodine are also monovalent.

The formulae of the compounds of the halogens with the two common alkali metals—sodium and potassium—are:

NaCl, NaBr, NaI and KCl, KBr, KI

The halogens have been shown to be monovalent. Inspection of these formulae indicates that sodium and potassium are similarly monovalent.

Again, having established the monovalency of the halogens, study of their compounds as set down in the formulae with other metallic atoms will indicate the valency of the latter: $MgCl_2$, $ZnBr_2$, CaI_2. Here two atoms of each of the halogens are combined with one atom of magnesium, zinc, and calcium respectively, and therefore it is deduced that these metals are all divalent (valency = 2).

Using the same method, in $AlCl_3$ aluminium is trivalent and in CCl_4 carbon is tetravalent (valencies of 3 and 4 respectively).

In the above examples and in a variety of similar common compounds, the valencies may be regarded as normal. There are, however, some familiar metals which exhibit a variable combining power in their molecular formulae. There are two chlorides of copper—cuprous chloride with the formula CuCl and cupric chloride or $CuCl_2$. Almost similarly there are two chlorides of iron—$FeCl_2$ and $FeCl_3$, ferrous and ferric chlorides respectively. In the copper compounds the metal is monovalent and divalent while in the second pair of examples the iron is divalent and trivalent.

The significance of the naming of these compounds is discussed below; here, however, it may be stated that these verbal and written names actually indicate very closely the valencies of the metals.

Equivalents. A chemical equivalent is defined as the number of grams (or any weight unit) of the substance under consideration which will combine with or replace, directly or indirectly, 1 g of hydrogen. For many purposes and for reasons beyond the scope of this work, 8 g of oxygen are used as the reference. The definition is clearly derived from the definitions of atomic and molecular weights.

In the examples and from inspection of the equations given earlier it may be deduced that the equivalent of a substance is its AW divided by its valency. Elements with more than one valency will therefore have more than one equivalent (Table 11.4).

TABLE 11.3

Reactants and AW	Resulting compounds and equivalents
Hydrogen (1) Oxygen (16)	H_2O 2 g H combine with 16 g O 1 g H combines with 8 g O Equivalent of oxygen = 8
Hydrogen (1) Carbon (12)	CH_4 4 g H combine with 12 g C 1 g H combines with 3 g C Equivalent of carbon = 3
Zinc (65·4) Oxygen (16)	ZnO 65·4 g Zn combine with 16 g O 32·7 g Zn combine with 8 g O Equivalent of zinc = 32·7

TABLE 11.4

Element	AW	Valency	Equivalent
Oxygen	16	2	8
Aluminium	27	3	9
Cuprous copper	63·5	1	63·5
Cupric copper	63·5	2	31·7
Ferrous iron	55·8	2	27·9
Ferric iron	55·8	3	18·6

STRUCTURE OF THE ATOM

Introduction. In the earlier discussions on the structure of matter it has been stated that the smallest "particles" in the chemical sense are the atoms, normally with a brief separate existence only, and the molecules of two or more atoms in combination; these latter may be regarded as the permanent units of substance.

It is further set down that the views of Newton and Dalton on the unique character of the atoms are still valid—again, in the chemical sense.

There are about ninety elements of natural occurrence and there are several others which appear in nuclear reactions; these may reasonably be termed artificial.

Reference to the table of elements placed in order of atomic number (pp. 240–3)—an explanation is given later—will suggest that this order is practically identical with an arrangement based on the sequence of increasing atomic weight. In fact the identity is not quite complete as is discussed below, but it is strikingly evident in the upper part of the table (see Table 11.5).

TABLE 11.5

AN	1	2	3	4	5	6	7	8	9	10	11
Element	H	He	Li	Be	B	C	N	O	F	Ne	Na
AW	1	4	7	9	11	12	14	16	19	20	23

This evidence led many, quite early in the history of the science, to speculate upon the possibility that all elements are constructed in some manner as multiples of a simple unit. Other than for hydrogen, the AW in most cases is twice the AN, while with the exceptions the departure is slight. It is therefore hardly surprising that many of the pioneer investigators suggested that all the elements are built, in some fashion, of hydrogen units. This deduction, or better, inspiration, is remarkably close in essence to modern theories of atomic structure.

Radioactivity. In 1896 H. Becquerel (1852–1908) observed that uranium compounds produced an effect on photographic plates similar to that of light although the plates were wrapped in the usual protective light-proof materials. Marie Curie (1867–1934) quickly devoted herself to study of this important discovery which she named "radioactivity", and her work culminated in the isolation of radium in 1898.

Radium, uranium, and the other radioactive elements emit three types of radiation:

(1) α (alpha) particles which are discharged by the radium atoms at a velocity of 10,000 miles a second and which are very close to the weight of the helium atom.

(2) β (beta) particles are projected with velocities which approach that of light. The weight of this particle is very small indeed when compared with the former.

(3) γ (gamma) rays which are not particles in the sense of the α and β discharges. They are similar to X-rays in their ability to pass through many inches of iron and two or three inches of lead.

The cathode rays. When an electric current is passed through a gas contained in a sealed glass vessel a fluorescence appears. This happening is said to have been observed as early as 1748 but well over a century later, E. Goldstein carried the experiment further. He progressively reduced the pressure within the glass tube containing the gas to the point when a distinctive type of fluorescence appeared at the end opposite the negative electrode or cathode. In 1876 he gave the name 'cathode rays' to the phenomenon.

Radioactivity and the atom. The study of the discharges from radioactive materials and of the cathode ray effect shattered very quickly the classic views on the indivisibility and indestructibility of the atom. The radioactive substances eject particles which can only originate in their atoms; the process is spontaneous and continuous and no alteration in the chemical and the physical circumstances interrupt the action.

With all the heavy radioactive elements a series of mutations occur—some of the intermediate products have a very brief existence—and the final result is lead.

The AN and AW of radium are respectively 88 and 226·1, those of lead are 82 and 207·2. Therefore, in becoming lead radium moves up the table of elements several places and discharges about 19 units of its mass.

α and β particles and cathode rays are deflected from their courses by magnetic fields while γ rays are not deflected. (The shifting of cathode rays on their paths to the television screen by changes in the electromagnetic fields through which they pass provides the familiar T.V. picture.) Therefore the α and β particles and cathode rays must be electrically charged but the γ radiation

is wave motion of the same type as light and X-rays differing in wavelengths or frequency.

As investigation continued and knowledge increased it became apparent that the structure of the atom is electrical in character and that three particles are present:

(a) *The proton* of unit positive charge and of approximately unit mass.

(b) *The electron* of unit negative charge and of mass about $\frac{1}{1800}$ that of the proton; this mass is so small that it may be disregarded for many purposes. Cathode rays and the β particles emitted by the radioactive elements are electron streams and thus identical.

(c) *The neutron* is electrically neutral and its mass is almost that of the proton.

Other than for hydrogen, groups of protons and neutrons form the centre or nucleus of the atom, and consequently the nucleus, is electrically positive. Groups of electrons equal in number to the protons occupy orbits around the nucleus, and since protons and electrons are electrically opposed, the atom is neutral.

The simplest structure, as is to be expected, is that of the hydrogen normal atom (the significance of normal is explained below under "Isotopes"); it consists of one proton as the nucleus and one electron in orbit.

Atomic number and atomic structure (Fig. 11.1). Atomic number was originally used merely to set down the sequence of the elements in order of atomic weights, but, as a consequence of the growth of knowledge of atomic structure, it now has a much greater significance. Atomic number indicates the number of protons and thus the number of unit electrical charges in the nucleus of the atom of the element under consideration. Further it is now apparent that the differences between AN and AW express the additional loading of neutrons on the nucleus. Atomic number may also be defined as the number of electrons in the structure but the nucleus is held to be more representative of its atom.

Atomic structure and its significance for AN and AW is better understood when set down in the form of a diagram. Elements from 1 to 10 are selected for this purpose (it is, however, necessary to state that no plane figure can really express a structure in space adequately and that the scale must for practical needs, be very much condensed). It has been said that if the nucleus of the hydrogen atom is enlarged to the size of a cricket ball the orbit of

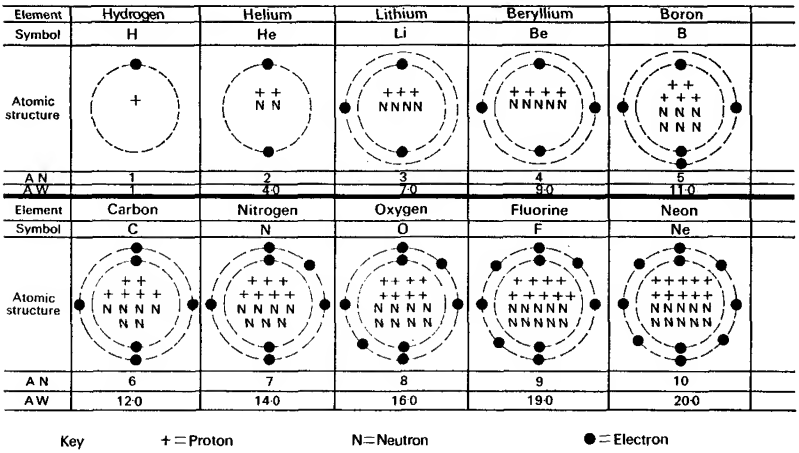


FIG. 11.1.

its electron will have a diameter of about 3 miles—the atom does appear to be very largely empty space.

Isotopes. Fractions of protons and neutrons are probably impossible and therefore if uniformity of all the atoms of any element is assumed, the atomic weights should be whole numbers only. However, fractional parts of AW are the rule rather than the exception, and this is more in evidence in the tables in very advanced works on chemistry where there is a great demand for as accurate a reading as possible. (It should be noted that atomic weights are constantly under revision.)

This apparent difficulty is explained by the existence of isotopes. An isotope is defined as a variety of an element which is completely identical in atomic number and in chemical properties with the standard but which differs in AW. This difference in AW is due to loading on the nucleus of more, or sometimes less, neutrons than in the case of what may be considered the normal. Since the AN and the chemical properties are determined solely by the electrical character of the nucleus and its accompanying electrons, the variation in the neutron content has little significance apart from AW.

The common gas chlorine has AN 17 and AW 35·5 and, as normally prepared or encountered, it consists of isotopes with eighteen and twenty neutrons respectively which give AW of 35 and 37. These varieties are mixed in proportions that give the accepted AW of 35·5.

The existence of isotopes also explains the apparent anomalies of the table where an element of greater AW precedes another of lower AW. Tellurium AN 52 AW 127·6 and iodine AN 53 AW 127; and argon AN 18 AW 39·9 and potassium AN 19 AW 39·1 are pairs of examples. In each case an isotope or isotopes are present in proportions which give the apparently irregular AW.

The heavier isotopes tend to nuclear instability and consequently to radioactivity. This is particularly marked with those elements towards the bottom of the table.

Isotopes of hydrogen. Three varieties of hydrogen are known: normal hydrogen of AW 1·0, sometimes called protium since its nucleus is a proton; deuterium of AW 2·0, the nucleus of which contains one proton and one neutron and is a deuteron; and tritium of AW 3·0, which has a nucleus of one proton and two neutrons and which is known as a triton.

Deuterium is present in ordinary water in the ratio hydrogen: deuterium = 6400 : 1. Deuterium oxide, D_2O, has all the properties of normal water other than its greater MW of 20·0. Heavy water is very important in nuclear power plants. It is separated from water by processes which demand an abundance of cheap electricity—hence the importance of Norway in this field.

Tritium, which is radioactive, may not occur in nature, and so far it has been prepared by bombardment of deuterium compounds by accelerated deuterons.

Ionization. The atom, as such, is electrically neutral since the positive charges on the nucleus are balanced by the negative charges carried by the electrons. Therefore if an electron is detached from or received by an atomic system, the latter ceases to be an atom and becomes a positive ion or negative ion respectively. The formation of ions by the detachment or reception of electrons is known as ionization.

The α particles, discharged by the heavy radioactive elements with a mass practically equal to the helium atom, are in fact nuclei of that atom and they are therefore helium ions of positive charge since their electrons are absent.

Structure and chemical combination. The formation of molecules by the coming together of two or more atoms is difficult to explain in terms of Dalton's atomic theory. It was observed that pairs of elements such as sodium and bromine readily form sodium bromide and, similarly, that chlorine and hydrogen combine spontaneously in sunlight to give hydrogen chloride or hydrochloric acid gas, while for long after the identification of some members of the helium–neon–argon group it was supposed that these gases had no chemistry since they appeared to form no compounds. It was therefore suggested that chemical combination is due to chemical affinity in the absence of which combination is impossible or rare. Explanations were sought, of course; among them was a proposal that the different atoms had different shapes and that some fitted together while others did not—like the pieces of a jigsaw puzzle.

In the light of present knowledge of atomic structure all chemical combination is explicable in terms of a transfer or displacement of an electron or electrons within a molecular system.

The chemical properties of the elements, including combining power, are derived almost wholly from the electronic configurations of their atoms and are ascribed more particularly to the uppermost electronic shells with the shell immediately below involved in a number of cases.

Apart from helium, which has two electrons in one shell only, all the inert gases have eight electrons in their outermost shells.

TABLE 11.6. SIMPLIFIED ELECTRONIC CONFIGURATION OF THE INERT GASES

Inert gas	Shells				
	K	L	M	N	O
Helium	2				
Neon	2	8			
Argon	2	8	8		
Krypton	2	8	18	8	
Xenon	2	8	18	18	8

Eight outer electrons, with two in the case of helium, appear to be associated with the extraordinary stability of the inert gases. The mechanism of chemical combination may be briefly stated to be due to the tendency of the atoms of the elements to assume this structure either singly or in association.

Three types of combination are usually recognized:

Electrovalency. In this type of bonding also called polar or ionic, an electron (or electrons) is transferred from one component to another to result in the formation of ions of opposite sign (Fig. 11.2).

In Fig. 11.2 lithium fluoride is selected as an example. It will be observed that the transference of the one outer electron from lithium to fluorine has several consequences:

(a) The lithium atom becomes an ion with positive charge.
(b) The fluorine atom becomes an ion with negative charge.
(c) The lithium ion has assumed the electronic configuration of helium.
(d) The fluorine ion has assumed the electronic configuration of neon.

The electronic structures of the sodium atom and the chlorine atom are:

	K	L	M			K	L	M
Sodium	2	8	1	Chlorine		2	8	7

The formation of sodium chloride is exactly analogous to that of lithium fluoride given above; the outer electron of the sodium atom is passed to the atom of chlorine. In the process the resulting sodium ion assumes the configuration of neon and the chlorine ion adopts the configuration of argon.

The electrical properties of the sodium and chlorine ions are exerted in all directions, and in the solid state these ions are placed

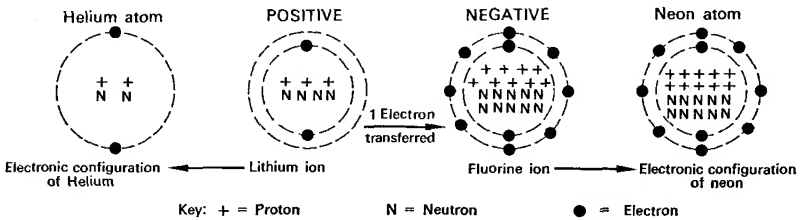


FIG. 11.2.

symmetrically and alternatively to form a lattice (Fig. 11.3). This structure extends at right angles to the rear and the pattern is repeated. This formation occurs with the closely related compounds, of great importance in photography, of sodium and potassium with bromine and iodine.

Electrovalent compounds in aqueous solution conduct an electric current and they are consequently known also as electrolytes and as such they possess properties of substantial influence in many industrial processes including printing.

Covalency. The molecules of the gases, the great majority of organic compounds, and water (but see below) are all examples of covalent compounds. Covalency is defined as the sharing of electrons in such a manner that both or all the components achieve the configuration of one or other of the inert gases (Fig. 11.4).

Cl^-	Na^+	Cl^-	Na^+
Na^+	Cl^-	Na^+	Cl^-
Cl^-	Na^+	Cl^-	Na^+
Na^+	Cl^-	Na^+	Cl^-

FIG. 11.3. The sodium chloride lattice.

In the molecule of hydrogen (Fig. 11.4a) the single electron contributed by each atom to the system confers the stability of helium; the six valency electrons of oxygen (Fig. 11.4b) are partnered by the two from the hydrogen atoms to provide the octet of the inert gases. Here it should be noted that water has in fact a very small ionization which has important consequences in chemical reactions. In methane (Fig. 11.4c) the four valency electrons of carbon and the four of the hydrogen atoms together also provide a shared stable octet.

Coordinate bonding. In covalent compounds all the component atoms have transferred electrons to the system, but in coordinate

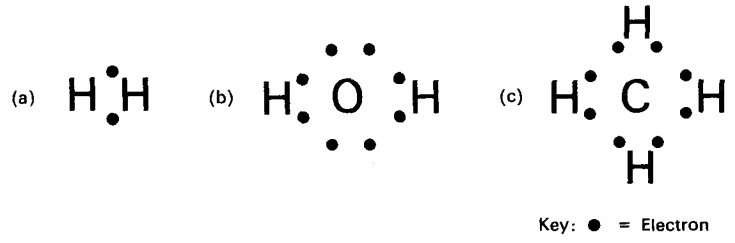


FIG. 11.4. Electronic configuration of some compounds (only the outer or valency shells of water and methane are shown).

compounds the shared electrons are contributed by one or some of the atoms only. This type of bonding is also called dative since one atom 'gives' the electrons, or semi-polar because the distribution of the electrons usually makes possible the union with other groups to form more complex molecules.

Sulphur dioxide is characteristic of one type of coordinate compounds while ammonia is representative of a rather larger class (Fig. 11.5).

As shown (Fig. 11.5a), in one manner of indicating a coordinate compound, the sulphur in sulphur dioxide has passed electrons to

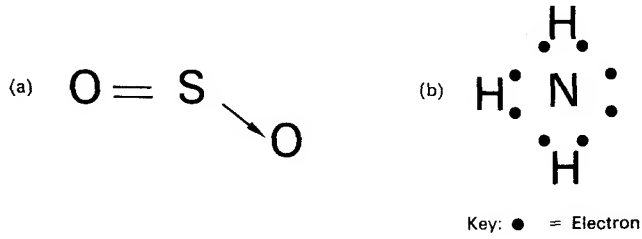


FIG. 11.5. Electronic configuration of (a) SO_2 and (b) NH_3 (only the outer or valency shell of ammonia is shown).

the oxygen atom arrowed while the double line (or bond) to the other means that its electronic configuration has not attained that of an inert gas; consequently the whole has polarity and it will quite readily combine with other groups. In the case of ammonia (Fig. 11.5b) two electrons are shown which, although they contribute to the octet of the nitrogen, are partially free to attract other radicles. The formation of the positively charged ammonium group NH_4 by the addition of an hydrogen ion is a example.

There are many compounds in which it is difficult to state that they are either covalent or coordinate; for instance, in the example above, ammonia may be considered to be intermediate in character.

Structure and valency. While valency has already been discussed in general terms it now becomes possible to show that its numerical aspects are related to the electronic configuration of the atoms taking part in the formation of a molecule; in brief, valency as a number is either the number of electrons in the uppermost shell of an atom or the number of electrons needed to complete the configuration of an inert gas in that shell. In lithium fluoride and sodium chloride, given as examples of electrovalency above, the electron lost by one component and gained by the other in each case indicates that lithium, sodium, fluorine, and chlorine all have valency of one. The metals magnesium, calcium, and zinc have atoms with two outer electrons and they are, in consequence, all normally divalent while aluminium is trivalent since its atom has three outer electrons.

The halogen group—fluorine, bromine, and iodine—in which each member has seven outer electrons and in which each normally accepts one electron to complete an octet, provides a further sequence of monovalent elements.

However, copper forms two types of compound; cuprous associated with its one outer electron and in which it is monovalent, and cupric, in which it is divalent, the additional electron being withdrawn from the shell below the uppermost. Iron also exhibits two normal valencies—its two outer electrons function in the ferrous compounds while, as in the case of copper, an additional electron is detached from a lower shell to form the trivalent ferric compounds.

In the examples cited above (they also appear in the earlier introductory section on valency) the valencies shown should be considered as typical since they are evident in the common or normal compounds of the elements discussed. However, it is necessary to note that other valencies, while rare, are possible. Thus, in principle, iodine could release some or even all of its seven outer electrons while iron could part with further electrons from its lower shell.

This brief explanation of the electronic aspects of valency has been confined to examples of electrovalency, but the explanation is valid for coordinate and covalency. In its compounds carbon is,

as expected in view of its four available electrons, all but invariably tetravalent and, almost as invariably, carbon compounds are covalent.

Oxidation and reduction. Oxidation is defined primarily as the addition of oxygen to an element or group or the subtraction of hydrogen from a compound. Reduction is conversely the removal of oxygen or the addition of hydrogen. These terms have acquired, however, a very much wider significance.

The elements whose atoms tend to release electrons are called electropositive since the loss of electrons leaves the residue positively charged, while those which tend to accept electrons are electronegative.

In general, hydrogen and the metals are electropositive while the non-metals, including oxygen, tend to be electronegative. Therefore oxidation in its wider sense means the addition of any electronegative atom or group to a compound or the subtraction of an electropositive atom or group. Similarly, reduction means the addition of electropositive or the removal of electronegative components.

The majority of chemical reactions involve both oxidation and reduction; thus in the typical action of an acid on a metal,

$$2HCl + Zn = ZnCl_2 + H_2,$$

the hydrochloric acid is reduced by the removal of the electronegative chlorine while simultaneously the zinc is oxidized by the addition of the two atoms of chlorine.

Oxidizing and reducing agents, i.e. substances which promote or accelerate these processes, are very important in the practice of chemistry.

The periodic table. A brief note on the periodic table appears above in the introductory matter on the elements. Mendeléeff, in the light of the information then available, arranged the elements in order of AW (with a few anomalies) in such a manner that those of like properties appear at regular intervals. In the versions of the table now current, AN is used in place of AW for the reasons given earlier in the matter on atomic structure.

In the table those elements which are placed in vertical columns

are the groups, the members of which possess very similar chemical properties—in some instances strikingly so—usually with steady variation as AW increases.

The most typical groups are the alkali metals of group I on the left and the halogens to the right.

In addition to this vertical relationship, neighbouring elements in the same horizontal periods often exhibit similarities; magnesium and aluminium with boron and carbon are pairs of examples.

Mendeléeff and his successors were able to predict, sometimes with striking accuracy, the properties of elements then undiscovered solely by reason of the position they were expected to occupy in the table.

Many variations of the periodic table are in use; that selected for this purpose is probably the easiest to understand (Fig. 11.6).

Transmutation of elements. It will be recalled that a principal purpose of the alchemists was the transformation of common or base metals into gold. Transmutation has indeed been achieved with some of the lighter elements, and those heavy elements beyond uranium may also be cited as examples of transmutation if not of creation. However, lead stubbornly remains lead, but the change of it or some other element to gold is no longer held to be impossible, but world finance may rest tranquil, at least for the present.

E. Rutherford (1871–1937) succeeded as early as 1919 in transforming nitrogen into oxygen. Examination of Fig. 11.1 will suggest that this would occur if a proton, a neutron, and an electron are added to the atom of nitrogen.

The simple apparatus used by Rutherford has been subject to enormous development in the intervening years; the cyclotron and synchrotron impart tremendous energies to particles and enable the study of nuclear reactions to advance at an incredible rate.

ACIDS, BASES, AND SALTS

These three groups include a vast number of inorganic and many organic compounds; the relation between them is admirably

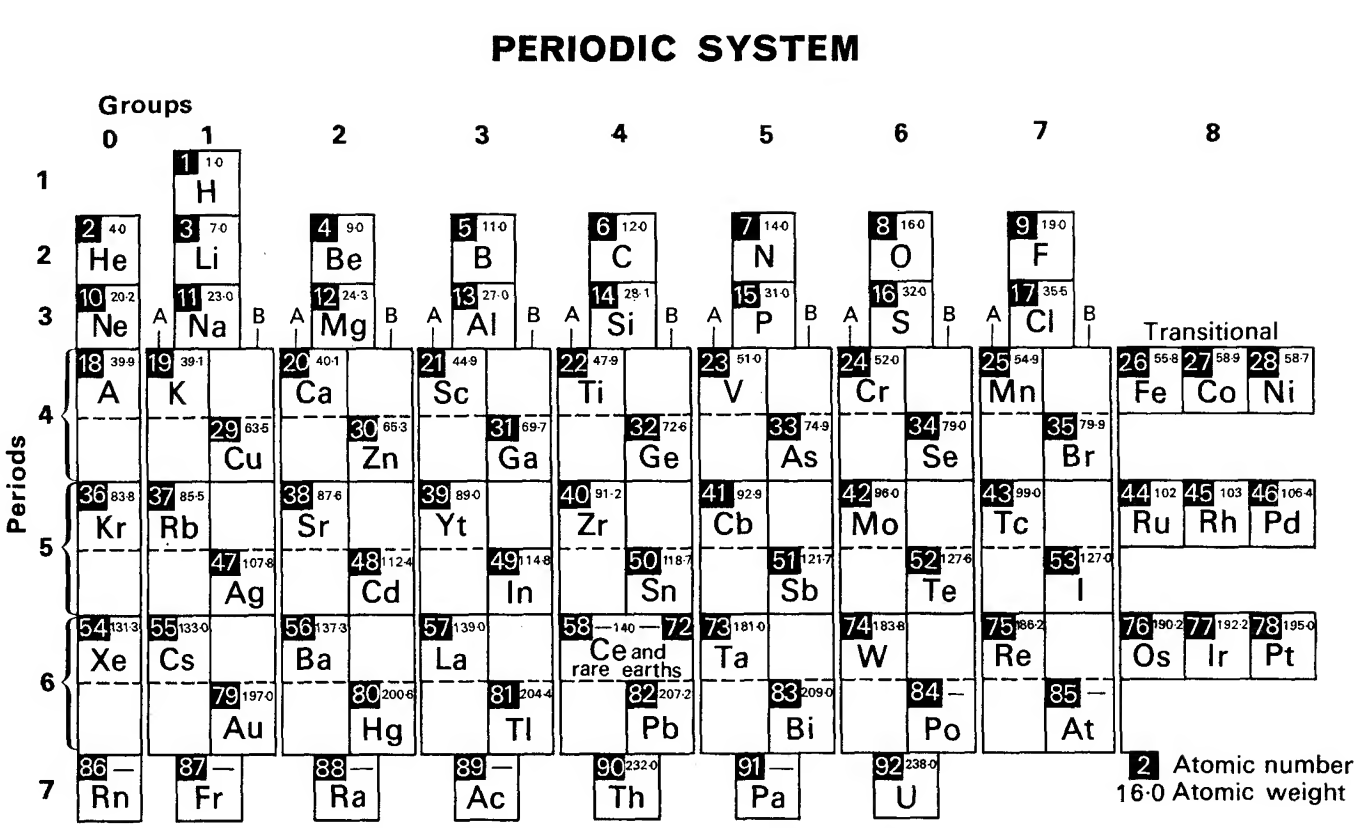


FIG. 11.6. This is a simple form of the table. The atomic weights of several of the heavier radioactive elements are still uncertain. The artificial transuranium elements are omitted.

expressed by the phrase in equation form: *Acid plus base equals salt and water.*

Acids. An acid is defined primarily as a compound which contains hydrogen; this hydrogen is replaceable by a metal in the typical acid reaction. More accurately an acid is a compound which releases hydrogen ions or protons in solution.

There are several less fundamental definitions; among them: *an acid is a substance which changes blue litmus to red,* and *an acid is a substance characterized by a sour taste as in vinegar,* which is a weak solution of acetic acid.

The three mineral acids probably outweigh in importance all the rest together; they are:

Nitric Acid	HNO_3
Hydrochloric Acid	HCl
Sulphuric Acid	H_2SO_4

The typical acid reaction of the definition is shown in Table 11.7.

TABLE 11.7

$2HNO_3$	+	Zn	=	$Zn(NO_3)_2$	+	H_2
$2HCl$	+	Zn	=	$ZnCl_2$	+	H_2
H_2SO_4	+	Zn	=	$ZnSO_4$	+	H_2

In each case part of the acid combines with the metal to form a salt (see below) and hydrogen gas is liberated. Zinc has been chosen as the metal. It should be observed that this metal is divalent—two nitrate radicles or two chlorine atoms are necessary in the compounds formed since each is monovalent while it is evident that the sulphate radicle is divalent.

Other divalent metals may be substituted for the zinc, magnesium, or calcium, for example, when the same numerical reaction would exist.

Although these reactions are described as typical there are very many other acids so feebly acidic that their behaviour in contact with a metal is so slow that it is difficult to detect. Nevertheless,

these compounds strictly conform to the definition of acids given above; representative of these are:

HCN	hydrocyanic or prussic acid
$HC_2H_3O_2$	acetic acid
H_2SO_3	sulphurous acid

Bases. A base is a compound of a metal with oxygen or hydroxyl (— OH). It should be noted that in this context the ammonium radicle (NH_4 —) is grouped with the metals since it appears to possess metallic properties.

It should further be noted that not all metallic oxides are bases and that non-metallic oxides in general have no basic properties.

The well-known hydrogen oxide (H_2O) is an example; others are carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O), sulphur dioxide (SO_2), and sulphur trioxide (SO_3). Many of the latter form acids when added to water.

A definition which states the chemical aspects is: *a base is a substance which reacts with a acid to give a salt and water only.* If the base has some solubility in water it changes red litmus to blue. Those bases with high solubility are known as alkalis, the most important of which are the hydroxides of sodium and potassium.

The majority of metallic oxides, particularly those of the heavy metals, have very low solubility but to the extent of such solubility they give hydroxides in water:

$$CaO + H_2O = Ca(OH)_2$$
$$MgO + H_2O = Mg(OH)_2$$

Salts. A salt is the result when the hydrogen of an acid is replaced by a metal. There is, however, a more important definition arising from the application of the verbal equation given in the introduction to this section—*acid plus base equals salt and water*—therefore a salt is the result of the action between an acid and a base, water being the other product. It is necessary to observe, however, that salts are rarely directly made by this method although the equation is ultimately involved in most or many cases.

TABLE 11.8

Acid	plus	Base	equals	Salt	and	Water
HCl	+	NaOH	=	NaCl	+	H_2O
HNO_3	+	KOH	=	KNO_3	+	H_2O
H_2SO_4	+	CaO	=	$CaSO_4$	+	H_2O
HBr	+	NH_4OH	=	NH_4Br	+	H_2O
HCN	+	KOH	=	KCN	+	H_2O
H_2CO_3	+	2NaOH	=	Na_2CO_3	+	$2H_2O$

NAMING OF COMPOUNDS

Introduction. From the earliest days of chemistry as an experimental science, attempts were made to give names to compounds which would indicate their composition. Many of these names survive, chiefly in industry, although with the advance towards accuracy some of them no longer serve the informative purpose originally intended. "Perchloride of iron" is well known in aqueous solution under that name for the etching of copper in the photo-engraving and photogravure processes. Hypo, an abbreviation of hyposulphite (of sodium), is in almost universal use for the fixing bath in photography.

But the first is not a perchloride and the fixer is not hyposulphite and, while it must be admitted that they function adequately under these obsolete names, they would behave just as sweetly as ferric chloride and sodium thiosulphate.

Naming of salts. Acids, bases, and salts, with oxides, hydroxides, and hydrides, constitute the majority of inorganic compounds, and of these it is likely that salts are the most familiar.

The actual or hypothetical formation of salts from acids and bases has been considered in the preceding section and, with this origin in mind, it is to be expected that the names of the majority of salts are divisible, like the salts, into two parts. The first part is derived from the base and it thus describes the basic (or metallic) radicle which includes ammonium as considered above under

"Bases". The second part is similarly derived from an acid and it indicates the acidic radicle.

In general acids fall into two groups—those with oxygen and those without oxygen (the word oxygen itself is derived from a Latin root meaning "acid", and all the earliest known acids did contain, or were believed to contain, oxygen; hence the name). Therefore the names of the acidic radicles of the salts are modified by suffixes which indicate the nature of the parent acid:

If the acid has no oxygen the suffix is *-ide*
If the acid contains oxygen and ends in *-ic* the suffix is *-ate*
If the acid contains oxygen and ends in *-ous* the suffix is *-ite*

The distinction in the terminations of the oxyacids is due to the differences in the oxygen content. The lower quantity of oxygen is shown by the *-ous* suffix and the higher by *-ic* (Table 11.9).

TABLE 11.9

Nitrous acid (HNO_2)	Nitric acid (HNO_3)
Sulphurous acid (H_2SO_3)	Sulphuric acid (H_2SO_4)
Chlorous acid ($HClO_2$)	Chloric acid ($HClO_3$)
Phosphorous acid (H_3PO_3)	Phosphoric acid (H_3PO_4)

The acids of phosphorus (Table 11.9) are often distinguished by the prefix *ortho-* since there are so many acids of this element that a rather complex nomenclature has been evolved; the names above are, however, those in common use.

Examples of salt names

Suffix *-ide* (see Table 11.10).

The suffix *-ide* is also used as the termination of simple binary compounds such as the oxides, hydrides and hydroxides (Table 11.11).

TABLE 11.10

Acid	Base	Salt
Hydrochloric (HCl)	Sodium hydroxide (NaOH)	Sodium chloride (NaCl)
Hydrobromic (HBr)	Potassium hydroxide (KOH)	Potassium bromide (KBr)
Hydrocyanic (HCN)	Potassium hydroxide (KOH)	Potassium cyanide (KCN)
Hydrogen sulphide (H_2S)	Sodium hydroxide (NaOH)	Sodium sulphide (Na_2S)

TABLE 11.11

Oxides	Hydrides	Hydroxides
Calcium oxide (CaO)	Phosphorus hydride (PH_3)	Lead hydroxide ($Pb(OH)_2$)
Nitrous oxide (N_2O)	Antimony hydride (SbH_3)	Zinc hydroxide ($Zn(OH)_2$)
Zinc oxide (ZnO)	Boron hydride(B_2H_6)	Ferrous hydroxide ($Fe(OH)_2$)

The metallic hydroxides and most of the metallic oxides have or tend to have basic properties.

Suffix *-ite* (Table 11.12).

TABLE 11.12

Acid	Base	Salt
Nitrous (HNO_2)	Sodium hydroxide (NaOH)	Sodium nitrite ($NaNO_2$)
Sulphurous (H_2SO_3)	Potassium hydroxide (KOH)	Potassium sulphite (K_2SO_3)
Chlorous ($HClO_2$)	Sodium hydroxide (NaOH)	Sodium chlorite ($NaClO_2$)
Phosphorous (H_3PO_3)	Aluminium hydroxide ($Al(OH)_3$)	Aluminium phosphite ($AlPO_3$)

Suffix *-ate* (Table 11.13).

TABLE 11.13

Acid	Base	Salt
Nitric (HNO_3)	Sodium hydroxide ($NaOH$)	Sodium nitrate ($NaNO_3$)
Sulphuric (H_2SO_4)	Calcium hydroxide ($Ca(OH)_2$)	Calcium sulphate ($CaSO_4$)
Chloric ($HClO_3$)	Potassium hydroxide (KOH)	Potassium chlorate ($KClO_3$)
Phosphoric (H_3PO_4)	Aluminium hydroxide ($Al(OH)_3$)	Aluminium phosphate ($AlPO_4$)

Suffixes to the basic radicle. When the metal has two common valencies the lower is indicated by the addition of the particle *-ous* to the stem of its name while the higher valency, in the same manner, terminates in *-ic* (Table 11.14).

TABLE 11.14

Lower valency	Higher valency
Cuprous chloride ($CuCl$)	Cupric chloride ($CuCl_2$)
Ferrous chloride ($FeCl_2$)	Ferric chloride ($FeCl_3$)

Prefixes. The composition of rather more complex compounds is suggested in many cases by additions, such as prefixes, to a portion of the name.

Per- means an excess or abnormal quantity of a component (Table 11.15).

TABLE 11.15

Normal compound	Abnormal compound
Hydrogen oxide (H_2O)	Hydrogen peroxide (H_2O_2)
Sodium oxide (Na_2O)	Sodium peroxide (Na_2O_2)
Barium oxide (BaO)	Barium peroxide (BaO_2)

All the above peroxides liberate the additional oxygen freely and therefore they are useful oxidizing agents. Hydrogen peroxide provides a considerable volume of oxygen weight for weight and it consequently has several well-known domestic (or cosmetic) uses. Inspection of Table 11.14 will confirm that $FeCl_3$ is the normal chloride of trivalent iron and that therefore the still popular "perchloride of iron" is a misnomer.

Thio- (Greek *theion* = sulphur) indicates that a sulphur atom has been substituted for another, usually oxygen, in the parent compound (Table 11.16).

TABLE 11.16

Parent compound	Thio-compound
Sodium sulphate (Na_2SO_4)	Sodium thiosulphate ($Na_2S_2O_3$)
Potassium cyanate (KCNO)	Potassium thiocyanate (KCNS)
Urea (organic) ($CO(NH_2)_2$)	Thiourea ($CS(NH_2)_2$)

Hypo- as a prefix to the name of a compound means 'under', 'lower', or 'below'. It will be sufficient to give as examples the names of some hypo acids (Table 11.17).

TABLE 11.17

Hypochlorous acid (HOCl)	Hypophosphorous acid (H_3PO_2)
Hypobromous acid (HOBr)	Hyposulphurous acid ($H_2S_2O_4$)

Salts of these hypo acids are well known although some of the acids may be described as hypothetical. It will be observed that the photographer's hypo is not a salt of hyposulphurous acid and that it is, in fact, a salt of thiosulphuric acid (but for all that the name hypo will endure).

Bi- is used as a prefix to indicate the hydrogen containing or acid salt of an acid with two replaceable hydrogen atoms (Table 11.18).

TABLE 11.18

Acid	Bi-salt
Carbonic (H_2CO_3)	Sodium bicarbonate ($NaHCO_3$)
Sulphurous (H_2SO_3)	Sodium bisulphite ($NaHSO_3$)
Sulphuric (H_2SO_4)	Sodium bisulphate ($NaHSO_4$)

There is a tendency to use more informative names for the above. Thus $NaHSO_3$ is better described as sodium hydrogen sulphite or sodium acid sulphite (acid because the hydrogen remaining in the compound confers acid properties on the whole).

Phosphoric acid, H_3PO_4, has three hydrogen atoms available for salt formation: these salts are systematically and thus informatively named (Table 11.19).

TABLE 11.19

NaH_2PO_4	Sodium dihydrogen phosphate
Na_2HPO_4	Disodium hydrogen phosphate
Na_3PO_4	Trisodium phosphate (or normal sodium phosphate)

Naming of organic compounds. The matter above applies mainly to the names of inorganic substances and, while some sections have limited applications to organic compounds, in general a self-contained system of nomenclature has been adopted for the much more complex organic chemistry which will be considered in the introduction to this branch of the science below.

CRYSTALLIZATION

It is likely that the majority of pure substances occur, or may be prepared, as crystals. The arrangement of the components within the molecule appears to determine the form of the crystal; thus

the cubic crystal of sodium chloride is a reflection of the lattice considered above.

All crystals are indeed classified into surprisingly few geometrical systems, and crystals of different substances belonging to the same system are described as isomorphous (i.e., of similar form) and this is often evidence of close chemical relationship.

However, there are many substances, including several elements, which occur in different crystal systems. These varieties of the same material are known as allotropes. Carbon and sulphur are characteristic; the former appears as diamond and graphite with markedly different physical properties; coke and charcoal were for long described as amorphous, i.e. shapeless, but they are now generally accepted as impure forms of graphite, the crystals of which are microscopically small. Solid sulphur appears in at least three crystal forms, while there are many more liquid and even gaseous allotropes.

Water of crystallization. Many substances have water combined in their molecules. Several of the salts given in the tables above are in this category, but the anhydrous form has been set down in the interests of simplicity and brevity.

This combined water as a hydrate is an essential component of the crystal, but is usually easily removed by heating. The residual substance is anhydrous, i.e. without water, and the original crystal structure is destroyed.

Many salts occur in two or more hydrated forms (see below), and in these and all other hydrates the character is indicated by a prefixed Greek numeral (Table 11.20).

TABLE 11.20

Symbol	Name
$CuSO_4.5H_2O$	Cupric sulphate pentahydrate
$FeSO_4.7H_2O$	Ferrous sulphate heptahydrate
$Na_2CO_3.10H_2O$	Sodium carbonate decahydrate
$Na_2CO_3.7H_2O$	Sodium carbonate heptahydrate
$Na_2CO_3.H_2O$	Sodium carbonate monohydrate

Efflorescence. A number of crystal hydrates tend to give up a part or even the whole of their water of crystallization in suitable conditions, i.e. when the vapour pressure of the hydrate exceeds that of the partial pressure of the water vapour in the surrounding air or, in effect, when the relative humidity is low. Common washing soda is commercial sodium carbonate decahydrate, and if this is freely exposed in very dry weather it will discharge all or most of its water and crumble to a white powder.

Deliquescence. Many substances will take in atmospheric moisture, some to the extent that they dissolve in the water they absorb. This phenomenon is more marked, again, in humid conditions, but deliquescence is more precisely defined as occurring when the partial pressure of the atmospheric water vapour is greater than that of a saturated solution of the solid in question.

A number of the compounds regularly used in graphic reproduction deliquesce very freely; among these are sodium and potassium hydroxides and ferric chloride, and their containers must be completely sealed; when weighing they should be exposed as briefly as possible.

SOLIDS, LIQUIDS, AND GASES

Some substances are well known in these three physical states; water exists as ice, a liquid, and as a gas, but in all the compound appears unaltered. There are, however, very many substances where the heat energy needed to effect the change from solid to liquid, and more particularly to gas, would result in decomposition.

The differences in these three states may be briefly said to be due to the differences in the energies of the molecules, atoms, or ions of the substance under examination and that the energy levels of these particles normally rises with rises of temperature.

In a gas the particles move with almost complete freedom, being restrained only by the very small forces exerted by the surrounding particles. Gases always fill the whole of the volume of their containing vessels.

A liquid retains its volume if the conditions are constant and it also takes the shape of its container but does not necessarily

fill it. The particles of a liquid move in respect of each other, but this movement is very much restricted by the forces of cohesion exercised by all the particles present. Liquids in general are, because of these forces, little compressible.

In the solid state free movement of the particles ceases, but there is vibration within the limits of the inter-molecular, -atomic or -ionic spaces, and therefore a solid retains its shape if undisturbed by external stresses.

It is evident that the transition from solid to liquid and to gas is effected normally by increasing temperatures which result in increasing the energy of the particles. Conversely, with decreasing temperatures energy declines until at absolute zero (— 273°C) it is nil.

SOLUTIONS

A solution is defined as a uniform intermingling of one substance in another, usually at the molecular, atomic, or ionic levels. While solutions are commonly understood to consist of a solid in a liquid, they may be made up of two or more substances in any of the physical states as liquid–liquid, solid–gas, solid–solid, or gas–liquid.

Solvent and solute. A solvent is that component of a solution which receives the solute; the solute is that which is dissolved. There are, however, many cases in which it is difficult to distinguish the components—alcohol and water for example.

Saturation. A solution is said to be saturated when, in the given conditions, the solvent cannot accept further solute, any addition being thrown down or precipitated.

Supersaturation. In certain conditions, such as lowering the temperature (see below) of a saturated solution and maintaining complete immobility, it is possible to achieve supersaturation in which more than the normal quantity of solute is carried by the solvent. However, if the conditions are disturbed, by movement for example, the excess solute is almost immediately precipitated.

Solubility. The maximum amount in grams which 100 g of a solvent will accept into solution is a means of expressing the

solubility of that solute in the given solvent in the stated conditions —chiefly of temperature. In the case of a gas–liquid solution, solubility is commonly expressed in terms of the volumes of gas dissolved in volumes of solvent, again at a given temperature. The same units of volume must, of course, be used in each case.

The solubility of substances in water generally increases with increases in temperature, but there are many important exceptions. The solubility of sodium chloride is hardly varied between the freezing and boiling points of water while that of calcium hydroxide, $Ca(OH)_2$, which is very low in any case, actually decreases with rise in temperature.

The differences in solubility of many common substances allows the separation of mixtures to be undertaken. Slow evaporation of the mixed solution will eventually reach the point when the substance of lower solubility is precipitated, normally in crystalline form, and this may be removed by filtration or by careful decantation.

Eutectic point. When polar seas freeze the ice is pure or very close to complete purity and, since in the process water is removed, the material in solution under the ice becomes more concentrated. If this phenomenon is observed in the laboratory and the temperature steadily reduced, the remaining liquid becomes a saturated solution and this will then freeze, in its turn, as a whole. This occurs at the eutectic point and at the eutectic temperature. It should be noted that the residual solution becomes finally a solid solution of definite composition which is determined by the nature of the solute or solutes and the solvent.

Study of the eutectic point and mixture is of great importance in the formulation of alloys including many printing metals; the latter are considered in the appropriate chapter of this book.

Two simple examples are appended to illustrate the subject (Table 11.21).

Colloids. A colloid is a substance more easily understood by example than by definition. Starch, albumen, glue, and gum are all typical of a class of colloid and they are all rather complex organic compounds.

A colloidal solution differs from the true solution of, for

TABLE 11.21

System	Temperature at eutectic point	Eutectic mixture
Water–sodium chloride	− 21·2°C	H_2O 76·4% : NaCl 23·6%
Zinc–cadmium	270·0°C	Zn 17% : Cd 83%

example, salts in water in that the particles are separable from the solvent by a semi-permeable membrane such as parchment although they pass freely through ordinary filter papers.

Many colloids are used as the vehicles which carry the light-sensitive substances in pure and applied photography.

Suspensions. The particles borne by a solvent in a suspension are very much larger molecular aggregations than the particles of a colloidal solution and, while colloids may be a single chemical compound, the solids of a suspension are usually mixtures of many materials; the mud carried by a river consists of earths, clays, and rock fragments. Again, while a colloid solution is normally stable, the particles of a suspension will settle if the container is undisturbed.

The distinction between a suspension, a colloid solution, and a true solution is almost wholly a matter of particle size. It is possible to set down a classification based on the latter although it should be considered as an approximation only (Table 11.22).

TABLE 11.22

System	Particle size
Suspension	Exceeding $\frac{1}{10,000}$ mm
Colloidal solution	Between $\frac{1}{100,000}$ and $\frac{1}{1,000,000}$ mm
True solution	Molecule, atom or ion

METALS: NON-METALS

Introduction. The distinction between metals and non-metals appears to be so evident that it may seem unnecessary to invite formal definitions, but there is hardly one of the more obvious properties of metals which cannot be matched by at least one non-metallic element. For example, metals have a characteristic lustre, are generally of high density, and the majority are good electrical conductors; among the non-metals, carbon (as graphite) and iodine are as lustrous as the metals; carbon as diamond has a very high density and graphite is a good conductor of electricity.

However, with these reservations in mind, it is possible to tabulate the physical and chemical properties of metals and non-metals as generalizations only (Tables 11.23 and 11.24).

TABLE 11.23. PHYSICAL PROPERTIES

Metals	Non-metals
Lustre; capable of mirror polish	Rarely lustrous; some with glassy surface
Ductile and malleable	Commonly brittle; many are gases
High density; the alkali metals have low density.	Low density
Conductors of electricity	Poor or non-conductors
Conductors of heat	Poor or non-conductors

TABLE 11.24. CHEMICAL PROPERTIES

Metals	Non-metals
Form one or more basic oxides	Oxides are acidic or neutral
Usually displace hydrogen from acids	Do not displace hydrogen
Hydrides of metals are rare and unstable	Hydrides are normal and stable

There is, perhaps, only one of the above properties of the metals which is wholly satisfactory: to be classed as a metal an element *must* form at least one basic oxide; no non-metal has a basic oxide (the ammonium radicle appears to be almost completely metallic as far as it can be observed). Nevertheless, a number of metallic oxides have both basic and acidic properties, i.e. they act as expected by the equation acid + base = salt + water or, in suitable conditions, they form part of the acidic radicle in many salts. It should be observed that the oxygen of the metallic oxide is also present, wholly or partially, in the acidic radicle (Table 11.25).

TABLE 11.25

Metallic oxide	Basic properties	Acidic properties
Zinc oxide (ZnO)	Zinc chloride ($ZnCl_2$)	Sodium zincate (Na_2ZnO_2)
Chromic oxide (Cr_2O_3)	Chromic chloride ($CrCl_3$)	Potassium chromate (K_2CrO_4)
Stannic oxide (SnO_2)	Stannic chloride ($SnCl_4$)	Sodium stannate (Na_2SnO_3)

This type of metallic oxide is usually described as amphoteric, but the parent element still conforms to the definition of a metal.

Metalloids. A number of elements possess both metallic and non-metallic properties; among them are arsenic, antimony, and bismuth. They are metals in appearance, but all form hydrides which, in the case of arsenic and antimony, are stable; that of bismuth is rather less so. On the whole the properties of the metalloids are weighted slightly in favour of those of metals. As is to be expected, their oxides are amphoteric.

Antimony is one of the components of type and stereo metals.

Electrolysis. When an electric current is passed through an electrolyte in solution or fused, i.e. in the liquid state, decomposition occurs; the final products depend upon the nature of the substances present. Electrolysis is used to obtain many highly

reactive metals from their salts and to manufacture important industrial materials.

Using graphite as the anode (the positive electrode) and an iron cathode (negative), molten sodium chloride is decomposed by the electric current, the positive sodium ions move to the cathode, while the negative chlorine ions pass to the anode. The latter discharge their extra electrons and thus become atomic chlorine, and the sodium ions receive electrons to assume the metallic state.

The passage of an electric current through a concentrated aqueous solution of sodium chloride gives a rather different result since water is present, but chlorine is still a product; the sodium formed at the cathode reacts immediately with the water giving sodium hydroxide and hydrogen while chlorine is evolved at the anode (Table 11.26).

TABLE 11.26

Original material	Ions present	Primary products	Final products
Sodium chloride	Na^+ Cl^-	Na Cl(atomic)	Na (metal) $Cl+Cl=Cl_2\uparrow$
Sodium chloride water	Na^+ Cl^-	Na Cl(atomic)	$2Na+2H_2O$ $2Na(OH)+H_2\uparrow$ $Cl+Cl=Cl_2\uparrow$

Electrolysis is also applied to the electrodeposition of metals. This is considered in Chapter 18.

CHAPTER 12

Hydrogen Ion Concentration: pH

Introduction. Although this subject forms part of the general body of chemical knowledge, a separate chapter is devoted to it in view of the great importance of its industrial applications and particularly of the increasing appreciation of this importance in printing processes.

Acids and bases. An acid has been defined as a substance which releases hydrogen ions or protons in solution (there are other definitions—see page 191).

The strength, i.e. the chemical activity, of an acid is determined by the availability of hydrogen ions and not by the hydrogen content of its molecule. Thus, taking hydrochloric acid as typical of the strong mineral acids and prussic or hydrocyanic acid as typical of the weak acids, each example has one hydrogen atom in its molecule, but while the former is probably wholly dissociated into ions

$$HCl \rightleftharpoons H^+ + Cl^-$$

the latter is very little dissociated

$$HCN \rightleftharpoons H^+ + CN^-$$

(the double arrows indicate dynamic equilibrium; the thick arrow shows the dominant direction).

Bases are similarly classified as strong or weak according to the availability of hydroxyl ions. The strong base (or alkali) sodium hydroxide is completely dissociated in solution

$$NaOH \rightleftharpoons Na^+ + OH^-$$

while the weak base ammonium hydroxide dissociates little—

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Hydrolysis. A salt is defined as the product, together with water, of the reaction between an acid and a base:

(a) $HCl + NaOH \rightleftharpoons NaCl + H_2O$

(b) $HCN + NH_4OH \rightleftharpoons NH_4CN + H_2O$

(c) $HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$

(d) $HCN + NaOH \rightleftharpoons NaCN + H_2O$

The right-hand sides of these equations show in effect solutions of salts in water; if the actions are considered as proceeding from right to left (all chemical actions are theoretically reversible), i.e. in the directions of the lower arrows, the effect of hydrolysis is seen and the character of each solution becomes evident (Table 12.1).

It is apparent that it would be possible to estimate the acid or alkaline character of salt solutions in terms of the nature of their components. This would, however, involve rather elaborate calculations and, consequently, a means of expressing what is required in terms of one component only has been evolved.

TABLE 12.1

Salt	Acid	Base	Character in solution
(a) Sodium chloride	Strong	Strong	Neutral (approximately)
(b) Ammonium cyanide	Weak	Weak	Neutral (approximately)
(c) Ammonium chloride	Strong	Weak	Acid
(d) Sodium cyanide	Weak	Strong	Alkaline (strongly)

Ionization of water. Water distilled to as near to absolute purity as possible is practically a non-conductor of electricity, i.e. it ionizes or dissociates very little indeed. Most natural and tap-waters conduct fairly freely because of their dissolved salts. Using the same symbolism to indicate this action

$$HOH \rightleftharpoons H^+ + OH^-$$

the lower arrow expresses a process which is so predominantly to the left that the quantity of hydrogen ions is 1/10,000,000 g in the litre. This is better stated in the more convenient form as 10^{-7} gram-ions per litre and, since each hydrogen ion must be accompanied by one hydroxyl ion, the latter is present in the same amount (the weights of these ions are practically the same as those of the hydrogen atom and the hydroxyl group respectively, and thus the actual quantities are $[H^+] = 1 \times 10^{-7}$ g/l and $[OH^-] = 17 \times 10^{-7}$ g/l.

Ionic product of water. The ionic product of water is $[H^+] \times [OH^-]$ (the square brackets may be taken as meaning quantity of) and this is numerically $10^{-7} \times 10^{-7}$, i.e. 10^{-14} (to multiply similar quantities raised to powers add the indices). This value is a constant if the conditions (chiefly temperature) are unchanged, and thus if hydrogen ion is increased by the addition of an acid or an acid salt, hydroxyl ion is decreased. For example, if $[H^+]$ is raised to

10^{-6}, $[OH^-]$ is reduced to 10^{-9} and the constant of 10^{-14} maintained. Similarly, if $[OH^-]$ is increased to 10^{-6}, $[H^+]$ is decreased to 10^{-8}.

Therefore it is possible to state the acidity, alkalinity, or neutrality of a solution in terms of the hydrogen ion content only.

The pH scale. pH literally is hydrogen ion exponent; it is defined as the common logarithm, with the sign reversed, of the hydrogen ion concentration in gram-ions per litre. Since a litre of pure water at normal temperature contains 10^{-7} g of hydrogen ions and 10^{-7} g-ions of hydroxyl, the liquid is neither acid or alkaline and pH 7 expresses neutrality, 7 being the logarithm of the concentration with the sign reversed, i.e. the negative is omitted and the positive implied. This device does result in the apparent paradox that as the number indicating pH value decreases the quantity of hydrogen ions, and consequently the acidity, increases (Fig. 12.1).

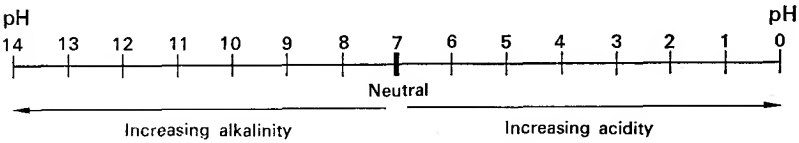


FIG. 12.1. A simplified form of the pH scale.

pH measurement. Methods for the determination of pH fall into two groups: (a) electric and (b) colorimetric.

Electric. The most precise means for the evaluation of pH are electric pH meters. These instruments are used for critical experimental work and for some refined industrial purposes; they are, however, rather expensive and need careful maintenance. It is beyond the scope of this work to consider in detail the complex character of these meters, but, briefly, it may be stated that the e.m.f. (usually expressed as voltage) of an electric cell rests largely upon the nature of the electrolyte in which the electrodes are immersed and that, in general, e.m.f. increases with the concentration of hydrogen ions. In the pH meter the solution under examination is used as a component of a cell and the pH of the solution is determined directly in terms of the hydrogen ions present.

Colorimetric. Many substances, mainly dyes, have a colour change at some point in the pH scale. The most familiar example is litmus which is red in acid solutions and blue in alkaline solutions. The change in colour occurs between pH 6·5 and pH 7·5—around the neutral point. Perhaps the most apparent colour shift is that of phenolphthalein which is colourless at pH 8·3 and below, and a striking red a little under pH 10. It should be observed that the change in phenolphthalein occurs wholly in the alkaline zone of the scale.

While colorimetry is strictly the measurement of colour it is also used in the present context for the evaluation of colours by matching or comparison with standard liquids or colour charts.

Some of the materials in use as indicators for pH purposes are shown in Table 12.2.

TABLE 12.2

Indicator	pH range	Colour change
Thymol blue	1·2– 2·8	Pink to yellow
Bromophenol blue	2·8– 4·6	Yellow to blue
Methyl orange	2·9– 4·0	Red to yellow
Bromocresol green	3·6– 5·2	Yellow to blue
Methyl red	4·2– 6·3	Red to yellow
Bromothymol blue	6·0– 7·6	Yellow to blue
Litmus	6·5– 7·5	Red to blue
Phenol red	6·8– 8·4	Yellow to red
Cresol red	7·2– 8·8	Yellow to red
Thymol blue	8·0– 9·6	Yellow to blue
Phenolphthalein	8·3–10·0	Colourless to red
Thymolphthalein	9·3–10·5	Colourless to blue

It should be observed that several indicators have two phases of colour change (an example is given in Table 12.2. Thymol blue completes its change from pink to yellow at pH 2·8; it remains that colour to pH 8·0 when the second change commences being complete at pH 9·6 when the indicator becomes blue.

It is rarely necessary to examine solutions at the extremes of the scale since these will usually be acids or caustic alkalis in fairly high concentrations.

BDH universal indicator. By the use of a single solution, prepared by the mixture of a number of specific indicators, it is possible to cover a wide pH range with distinctive colour changes throughout the values from pH 3·0 to pH 11·0.

Indicator papers. The test sample may be evaluated in the simplest possible manner by means of indicator papers. These are supplied in booklets made up of slips of pure filter paper containing the appropriate dyes, each paper being rather more than 6 cm by 1 cm. They are available in both narrow and wide ranges of the pH scale.

In use a wide range paper is lightly immersed in the solution under examination and the colour which appears is matched with a colour patch on the booklet cover. The pH value obtained is checked by means of one, or perhaps two, narrow range papers which are effective around the first estimated value.

However, while indicator papers meet a need they have obvious disadvantages. It is often difficult to compare the wet colour of the paper with that of the dry printed patches, and it becomes all but impossible to evaluate coloured, particularly deep coloured, solutions (see below).

Indicator liquids. These afford a much more delicate means of estimating pH values. Indicator liquids are also available in wide or narrow ranges. In practice the colour changes produced in the indicator by the test sample are compared with one or all of the buffer tubes which are usually in sets of about nine. These latter are sealed tubes containing acid and alkaline solutions to each of which an indicator appropriate to the set has been added; they are buffers since the solutions are prepared in such a manner that variations in their hydrogen ion concentrations are inhibited or retarded.

For use, one drop of universal indicator is added to about 3 cc of the sample. The resulting colour is referred to the chart on the indicator bottle or, better, to a larger separate chart, and an approximate pH value obtained. A specific or narrow range indica-

tor is used in the same manner, but the colour change is matched with one of a set of buffer tubes. Where the colour appears to be between two of the tube colours, a pH value may be interpolated.

The BDH comparator. While the above procedure is effective enough for many purposes, the use of the simple comparator adds much to both accuracy and flexibility. This instrument is made of a black plastic; it has ten circular holes to receive the test solutions and the buffer tubes. The holes are arranged in five pairs, the outer holes being merely used to support the buffers temporarily; the three inner pairs serve for viewing through slots in the comparator structure for the purpose of observation of test

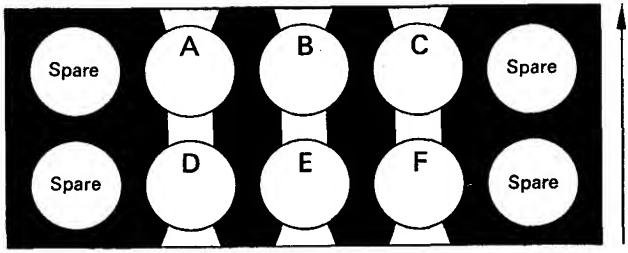


FIG. 12.2. The BDH comparator head.

samples with added indicator and the buffers in the same conditions (Fig. 12.2).

The test solution is added to each of three tubes; these are placed in spaces *A*, *B*, and *C* as shown in Fig. 12.2. An indicator is dropped into the solution in the tube in space *B* only. A standard buffer is inserted in spaces *D* and *F*; that between them (*E*) is occupied by a tube of distilled water. Observation is made to north light (in the northern hemisphere), or to good reflected white light, in the direction of the arrows. It should be apparent that the liquid and the buffers are seen in identical conditions. The buffer tubes are replaced one by one until a match is obtained.

In this type of investigation it is important that all the tubes should be as nearly alike as possible, and they should be of "hard" glass since common soda glass is appreciably soluble in water.

This apparatus permits the examination of coloured solutions; indeed, in many cases colour, especially if complementary, is actually an advantage—it makes observation very much easier.

The Lovibond comparator. This instrument is a further refinement in pH colorimetry in which the colour given by the indicator in the sample is matched with that of a glass filter.

The comparator has a hard plastic case with a hinged cover to

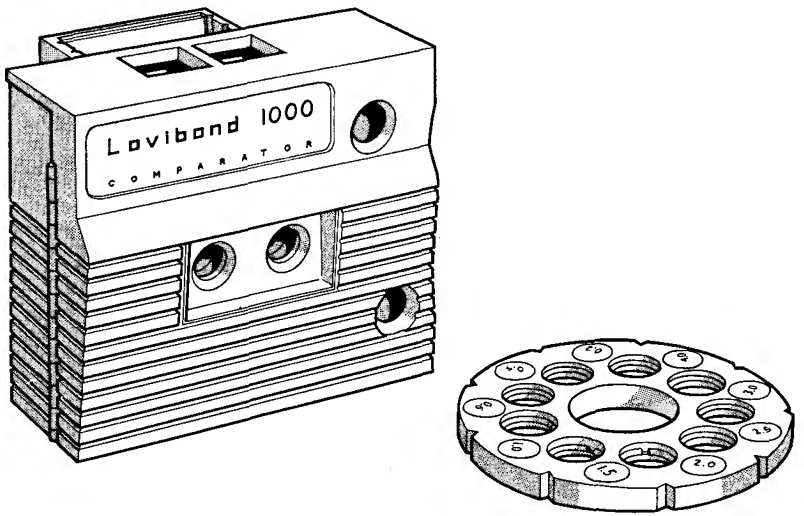


FIG. 12.3. A Lovibond comparator and disc.

receive the discs which carry the filters. Most of the discs have nine numbered filters graduated in steps of pH 0·2 to show the colour changes over the pH range of a single indicator. The test solution is added to two glass containers which may be rectangular cells or tubes.

In operation the indicator of the range selected is added to the righthand container and the disc with the corresponding colours and pH values inserted in the carrier. The disc is rotated until there is as near as possible a match between the test liquid and the

filter; since the latter is viewed through the liquid the method ensures that the colour given by the indicator and the filter are examined in precisely similar conditions, any inherent colour of the test sample being present at both apertures (Fig. 12.3).

Printing kit. The Lovibond comparator has been adapted, with the co-operation of PIRA, to the particular needs of the industry. Filter discs are provided to meet each of the many purposes together with accessories which are considered in the appropriate sections.

pH in printing. The importance of controlling the pH values of very many of the materials used in the industry is becoming increasingly recognized; it may, indeed, be stated that all solutions used in all industrial processes and many inherently solid materials which are capable of absorbing moisture ought to be examined and specified in terms of the pH values at which they are most effective.

The applications of pH to printing are considered in the chapters which deal with specific processes.

CHAPTER 13

Chemistry: Organic

Introduction. It was long supposed that substances derived from plants and animals had properties which, in some mysterious manner, distinguished them from those of mineral origin. This view should have been shattered by the experiment in 1828 of F. Wöhler (1800–82) in which the undoubted inorganic ammonium cyanate was converted to the equally undoubted organic urea, a constituent of mammalian excreta (see below under "Isomerism"), but the idea of the extraordinary properties survived here and there almost into this century.

Organic chemistry is defined as the science of the compounds of carbon, but the oxides and sulphides of that element with the carbonates are all but excluded. It may appear remarkable that the compounds of one element of the ninety-two are selected but carbon does possess some unusual qualities:

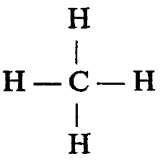
(a) It is almost invariably tetravalent; almost all organic compounds are covalent.
(b) It is able to form linkages with itself, atom by atom, to give compounds of great complexity and wide variety. The numbers of such compounds appear to be all but infinite.

Strictly, carbon is not alone in the property given under (b) since several elements, notably carbon's close relative silicon, are able to form auto-linkages, but in no case is it so fully developed as in the case of carbon.

Very few elements enter into the formation of organic compounds; many thousands consist of carbon and hydrogen only and many more of carbon, hydrogen, and oxygen. Nitrogen enters into the composition of a large number of important compounds while phosphorus, sulphur, and the halogens are of rarer occurrence—sulphur, chlorine, and bromine appear largely in compounds which may be called synthetic in that they do not form part of many naturally occurring substances.

It is necessary to emphasize that, in spite of the almost unique properties of carbon, all the laws of chemistry apply to all its compounds.

Structural formulae. The simplest organic compound is methane which has the molecular formula CH_4. Since the tetravalency of carbon and the monovalency of hydrogen may be accepted as established, methane is more adequately represented by the graphic formula

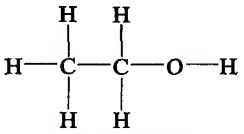


in which the linkages of the hydrogens to the carbon atom are shown by valency bonds. It is desirable to state, however, that the methane molecule is extended in space; the plane figure above is merely a compromise made necessary by the surface of the paper.

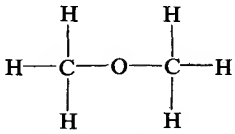
The results of the analysis of an inorganic compound are usually enough to enable an acceptable formula to be set down, H_2O, $FeCl_3$, MgO, etc., but more is needed in the field of organics. The empirical formula of ethyl alcohol or ethanol is C_2H_6O—this gives the composition without any information on structure. Methyl ether or dimethyl ether also has the empirical formula C_2H_6O, and therefore these substances have the same molecular weight and composition although they differ in almost all their properties. However, further investigation indicates that the alcohol has the hydroxyl group, — OH, while this is absent in the ether. It thus becomes possible, using the principles applied above to

P.B.S.—H

methane, to establish the structures of these compounds and to write their fully informative graphic formulae:



Ethyl alcohol



Methyl ether

While this is intended to stress the importance of a knowledge of structure, these two compounds are also examples of isomerism which is considered in some detail below.

DIVISIONS OF ORGANIC CHEMISTRY

Two broad divisions are accepted: these are based primarily on structural types—aliphatic or open-chain and cyclic or closed-chain compounds. In the first the molecule is extended as a line or chain. While this line may be, and very often is, branched, compounds are known with thirty or more carbon atoms forming an unbranched chain. In the second the basic molecule is, as is implied by the term cyclic, a closed ring. Benzene, perhaps the simplest example, has six carbon atoms joined by valency bonds in such a manner that they form an unbroken figure with one atom of hydrogen attached to each carbon.

The cyclic compounds are further subdivided into groups according to the character of the elements forming the ring and to their number.

Substitution. A special property of organic compounds, rarely encountered in inorganic substances, is that of substitution i.e. the exchange of one or some of the components attached to a carbon nucleus—in this context nucleus means the carbon skeleton of the structure.

Methane reacts spontaneously with chlorine in sunlight, and if calculated amounts of chlorine and methane are made available, one, two, three, or four of the hydrogen atoms may be replaced

successively by chlorine to give four distinct compounds. (Table 13.1.)

TABLE 13.1

Molecular formula	Physical state	Systematic or formal name	Other name
CH_4	Gas	Methane	———
CH_3Cl	Gas	Monochloromethane	Methyl chloride
CH_2Cl_2	Liquid	Dichloromethane	Methylene chloride
$CHCl_3$	Liquid	Trichloromethane	Chloroform
CCl_4	Liquid	Tetrachloromethane	Carbon tetrachloride

It is to be noted that what is usually considered to be the most informative name expresses each of these compounds as substitution products of the parent methane.

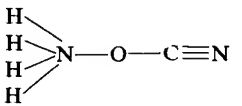
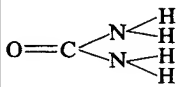
Bromine reacts similarly, although not so freely, to give a group of closely related compounds.

Saturation. The tetravalency of the carbon atom has been stressed and when all the available valency bonds have been filled the substance is said to be saturated; otherwise, with unoccupied valency positions, the compound is unsaturated. This condition is quite distinct from the variable valency exhibited by such elements as copper and iron—in the compounds $FeCl_2$ and $FeCl_3$ (ferrous and ferric chloride)—the valencies of di- and trivalent iron are fully saturated, but unsaturated organic compounds in general readily accept the addition of atoms to attain saturation. Examples of a number of important groups of unsaturated compounds appear below.

Isomerism. When two or more distinct compounds which have the same empirical molecular formula but which differ in the position of the components within the molecule, they are said to be isomeric. It is evident that differences in structure account for the differences in properties.

One pair of examples of isomerism—ethyl alcohol and methyl (or dimethyl) ether—has been given above but ammonium cyanate and urea have merely been cited; they do, indeed, provide an even more striking example (Table 13.2).

TABLE 13.2

Empirical formula	Possible graphic formula of ammonium cyanate	Graphic formula of urea
N_2CH_4O		

In the cyanate two of the very variable valencies of nitrogen are shown; only the lower of these occurs in urea.

It has been calculated that the numbers of isomers possible with the molecular formula $C_{13}H_{28}$ is 802.

Homologous series. A characteristic of organic compounds which hardly exists in other than a rudimentary form in the inorganic field is the existence of groups of similar chemical type which exhibit steady gradations in properties and in which all the members may be adequately represented by single formulae, partly mathematical in content.

The first of these homologous series is the paraffin hydrocarbon group which is considered in the matter following.

ALIPHATIC COMPOUNDS

Saturated hydrocarbons. The paraffins. Few elements form more than two hydrides; there are thousands of possible compounds of carbon and hydrogen—the hydrocarbons—and almost all of these are believed to be known.

The simplest member of the paraffin family is methane, CH_4, and it is, perhaps obviously, the only hydrocarbon with a solitary carbon atom in its molecule. It is present in coal-gas; it occurs over marshlands as marsh gas where it is a product of wet and decaying vegetation; it is the principal constituent of natural gas which is becoming increasingly important as a fuel and as a raw material in the chemical industry. Methane as fire-damp has long been one of the many hazards of coal-mining and it is the lowest fraction present in the majority of petroleums.

The atmospheres of several of the remote planets have been shown to be composed largely of methane, and it is held by some geologists that the earth's atmosphere in the very distant past also contained the gas but that it has been slowly withdrawn by the developing plant and perhaps some animal life.

Preparation of methane. There are several methods for the laboratory preparation of methane and perhaps the simplest is the reaction of aluminium carbide with water:

$$Al_4C_3 + 12H_2O = 4\ Al(OH)_3 + 3CH_4$$

The chlorine-substituted compounds of methane have been mentioned above; there are several other compounds possible by substitution by other radicles on this simple single carbon nucleus, but space and the scope of this work do not permit their consideration here.

Ethane (C_2H_6). This gaseous hydrocarbon resembles methane in many of its properties including chlorine, and to a lesser extent, bromine substitution. It also occurs in petroleum and natural gas.

The paraffins. Methane and ethane are the first two members of this very important series (Table 13.3). These and the majority of the natural members occur in petroleum, i.e. rock oil, now found in so many parts of the world, sometimes in regions once deemed economically without hope such as the deserts of Arabia. Some of these states are among the richest in the world because of the presence of this valuable oil—one wonders what will happen when the wells dry up.

The paraffins with twenty-three to about twenty-eight carbon atoms are the principal constituents of paraffin wax used for

TABLE 13.3. THE PARAFFIN SERIES, C_nH_{2n+2}

Molecular formula	Name	State at room temperature	Main uses
CH_4	Methane	Gas	Lighting and heating. Raw materials
C_2H_6	Ethane	Gas	
C_3H_8	Propane	Gas	
C_4H_{10}	Butane	Gas	
C_5H_{12}	Pentane	Liquid	Petrol (gasoline) Lighting and heating (paraffin oil—kerosene)
C_6H_{14}	Hexane	Liquid	
C_7H_{16}	Heptane	Liquid	
C_8H_{18}	Octane	Liquid	
C_9H_{20}	Nonane	Liquid	
$C_{10}H_{22}$	Decane	Liquid	
$C_{17}H_{36}$	Heptadecane	Solid	Petroleum jelly (vaseline), Lubricating oils, Fuel oils (diesel)
$C_{18}H_{38}$	Octadecane	Solid	
$C_{20}H_{42}$	Eicosane	Solid	

candles and for mounting biological and other specimens. The largest molecule of a paraffin hydrocarbon is a synthesized product stated to be of MW 1318 and of molecular formula $C_{94}H_{190}$.

Inspection of any of the paraffins in Table 13.3 will confirm that the general formula given at the head does indeed represent the whole series.

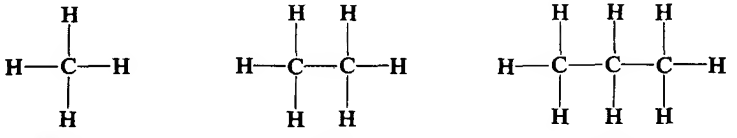
All members of the series burn when ignited in the presence of oxygen (from air or otherwise), but they are, in general, characterised by inertia in the chemical sense. The name of the series is, indeed, derived from *par(um) affinis*, i.e. 'little affinity', which aptly indicates this quality.

Fractional distillation of petroleum. The crude oil as it is obtained from the earth is a viscous black or dark-coloured liquid. The constituents are separated in a fractionating tower which differs little in principle from some laboratory distilling apparatus. The cruder impurities present in many petroleums are separated by

filtration under pressure; the raw oil is then led into the tower or column which is compartmented—but not sealed—by baffles inclined slightly downwards at their outer margins. The oil is subjected to progressive rises in temperature and at each stage the appropriate fraction comes off close to its boiling point; further processes of distillation are carried out when the consideration is the purity of the final product.

Before the advent of the internal combustion engine the principal product of the fractional distillation of petroleum was paraffin oil or kerosene which was for long a most important material for lighting and which was very much in use for heating including cooking. The lighter fractions were deemed to be almost worthless. Today some of these once discarded materials—petrol or gasoline —are the chief reason for the continuous search for new sources of petroleum.

Isomerism of the paraffins. Examination of the first three members of the series, set down as their graphic formulae, will indicate that no isomers are possible:

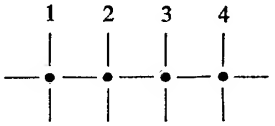


Methane Ethane Propane

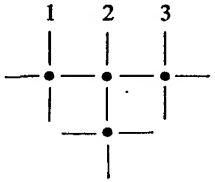
This is to state that it is not possible to arrange these formulae in any other manner and maintain the standard valencies of carbon and hydrogen. This may, perhaps, be more readily appreciated if the carbon nuclei alone are shown since the C — C linkage is essential to the system:

Ethane Propane

The first member of the series in which an isomer is possible is butane with four carbon atoms:



Normal butane



Isobutane

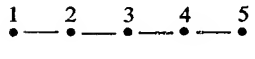
Thus normal butane—the adjective is usually shown as its initial in lower case roman—has a straight chain of four carbon atoms while isobutane—the prefix also in roman—has a chain of three carbons and one branch.

It is possible to use abbreviated structural formulae for compounds of this type:

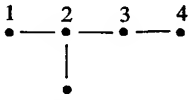
$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_3$ n-Butane

$CH_3 \cdot (CH) \cdot CH_3 \cdot CH_3$ Isobutane

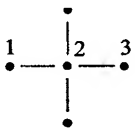
In the same manner pentane is shown to stand for three isomers:



n-Pentane



Isopentane



Neopentane

Here *n*-pentane has a carbon chain of five, isopentane has four, and neopentane with its chain of three in two directions may be said to be symmetrical. In the above, the nuclei only appear since these are sufficient to establish the existence of the isomeric pentanes. It should be observed, however, that in isopentane the branched carbon atom attached to carbon two could equally have

been attached to carbon three without resulting in a structural difference.

Chemically, the isomeric paraffins do not markedly differ, but all exhibit physical differences such as variations in melting and boiling points.

Motor-spirit. As is apparent in Table 13.3, petrol or gasoline consists principally of hexane, heptane, and octane, but other fractions are likely to be present in small quantities. Some motor spirits have alcohol or benzene as additional components for which special advantages are claimed.

While the greater part by far of the petrols available are petroleum products, many countries of no or limited petroleum resources have encouraged the production of motor spirit wholly or partly from (a) the low temperature distillation of coal, (b) the hydrogenation of coal, and (c) the use of ethyl alcohol. (a) and (b) are a feature of states like the United Kingdom with an abundance of coal while France is first or, perhaps alone, among those that insist upon the addition of alcohol distilled from the overproduced wine.

Process of cracking. In order to increase the quantities of available motor spirit the disruption or cracking of the longer chain and less volatile members of the paraffin series is widely practised, and these fractions are, in any case, of much lower commercial importance. Cracking is achieved by the subjection of these higher fractions to temperatures well above their boiling points. The action may be shown in a form which should be regarded as a rather uncertain indication of the actual process:

$$\underset{(\text{BP } 252^\circ\text{C})}{C_{14}H_{30}} \xrightarrow{500^\circ C} C_7H_{16} + C_7H_{14}$$

It will be observed that the second product is an unsaturated hydrocarbon; further disruption may occur by detachment of one carbon atom and, in any case, the existence of small quantities of an unsaturated material in a motor-spirit is acceptable:

$$C_7H_{14} \longrightarrow C_6H_{14} + C$$

Octane number. The tendency of a car or motor-cycle engine to 'knock', i.e. to premature ignition under compression, is more apparent with certain grades of motor-spirit. The majority of internal combustion engines are more efficient with high compression but this increases the tendency to knock. Therefore some specification is necessary to define the quality of motor-spirit; octane number is a means of expressing this quality.

In general the branched-chain paraffins among the fractions used for petrol are superior to the normal paraffins in their anti-knock properties; iso-octane and n-heptane are employed as criteria of the extremes of anti-knock and knock respectively. Octane number indicates the knock produced by a mixture of iso-octane and n-heptane, expressed as the percentage of the former in the mixture, which is the equivalent of the knock of the motor-spirit under test.

There are several additives which tend to eliminate knock; among them are benzene, alcohol, and organic lead compounds; the latter, however, are suspect on account of the small quantities of poisonous materials in the exhaust gases.

In the United Kingdom the British Standards Institution has introduced a system of grading which indicates the quality of the motor-spirit, including its anti-knock properties, by the number of stars shown on its pump.

Alkyl radicles. The roots of the names of the paraffins are used to designate the corresponding member of other aliphatic series with the addition of a suffix proper to the series. While there are slight departures, particularly with the lower members, the use of these radicles is almost fully systematic. The termination *-yl* is attached to the paraffin stem to indicate an alkyl radicle and for members of other series another suffix is substituted for *-yl* or a descriptive word is used with the radicle (Table 13.4).

It should be observed that apart from the lower members, the stems of the Greek numerals are employed to signify the paraffins and the radicles derived from them.

TABLE 13.4. ALKYL RADICLES, C_nH_{2n+1}

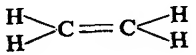
Parent hydrocarbon	Alkyl radicle
Methane (CH_4)	Methyl (CH_3 —)
Ethane (C_2H_6)	Ethyl (C_2H_5 —)
Propane (C_3H_8)	Propyl (C_3H_7 —)
Butane (C_4H_{10})	Butyl (C_4H_9 —)
Pentane (C_5H_{12})	Amyl (C_5H_{11} —)
Hexane (C_6H_{14})	Hexyl (C_6H_{13} —)
Heptane (C_7H_{16})	Heptyl (C_7H_{15} —)
Octane (C_8H_{18})	Octyl (C_8H_{17} —)

UNSATURATED HYDROCARBONS

The olefin series. The paraffin series has been considered rather fully since it appears to be the best representative of the aliphatic groups of compounds in respect of its wide range, commercial importance, the significance of its nomenclature, and the regular, if slight, gradation in properties as the series is ascended.

Since this is intended to be merely an introduction to the vast field of organic chemistry a few other aliphatic types are treated in brief only.

The general formula of the olefin series is C_nH_{2n} and inspection will confirm that the carbon nuclei cannot be saturated; the series is limited in range and it is probable that no member occurs naturally. Therefore the sources are principally the cracking of paraffin hydrocarbons from petroleum and from the coal-gas produced by the destructive distillation of coal. Since the olefins are unsaturated they are characterized by the free addition of very many elements and radicles and they are consequently of great industrial importance. The most valuable member is the first, ethylene. The structure has been the cause of considerable controversy but it is probable that the most satisfactory presentation is



this may be shown briefly as $CH_2 : CH_2$ (Table 13.5).

TABLE 13.5
SOME MEMBERS OF THE OLEFIN SERIES, C_nH_{2n}

Molecular formula	Systematic name	Usual name
C_2H_4	Ethene	Ethylene
C_3H_6	Propene	Propylene
C_4H_8	Butene	Butylene
C_5H_{10}	Pentene	Amylene
C_6H_{12}	Hexene	Hexylene

The termination *-ene* normally indicates a compound with one double bond to the molecule; this point of unsaturation is signified by the double line of the graphic formula and by the colon of the abbreviated formula of ethylene above. It is necessary, however, to remark that this termination appears in benzene and many related compounds without bearing quite the same meaning.

Diolefins. All the olefins properly so called have, as is stated above, one double bond only; there are several important compounds which possess two double bonds to the molecule. Butadiene, $CH_2 : CH . CH : CH_2$, is used in the manufacture of synthetic rubber, while the closely related isoprene, $CH_2 : CH . C(CH_2) : CH_2$, is the chief constituent of the natural substance.

The acetylene series, (C_nH_{2n-2}). The members of this series exhibit a higher degree of unsaturation than the olefins. The first and only important member is acetylene itself. The generally accepted structure is $HC \equiv CH$ with a triple bond linking the carbon atoms. This type of unsaturation confers a high chemical activity and, as in the case of the olefins, a ready formation of addition compounds. Further, since there is danger of explosion in the transport as a gas under pressure, acetylene is carried as a solution in acetone—the latter under compression will accept 300 times its own volume of the gas. It is almost certain that acetylene does not occur in nature and thus manufacture must be under-

taken. Among the many processes is the reaction between calcium carbide and water:

$$CaC_2 + 2H_2O \longrightarrow CH : CH + Ca(OH)_2$$

The acetylene gas produced in this manner was once widely used as an illuminant for bicycle and car lamps, since it burns with an intense and almost white flame.

Monohydric alcohol series, (C_nH_{2n+1} OH) (Table 13.6). The replacement of one of the hydrogen atoms of a paraffin by the

TABLE 13.6
SOME MONOHYDRIC ALCOHOLS, $C_nH_{2n-1}OH$

Formula	Usual name	Systematic name
CH_3OH	Methyl alcohol	Methanol
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	Propyl alcohol	Propanol
$CH_3(CH_2)_3OH$	Butyl alcohol	Butanol
$CH_3(CH_2)_4OH$	Amyl alcohol	Pentanol

hydroxyl, — OH, radicle would result in the corresponding member of this series—monohydric because one hydroxyl only is present. The most important member of the series is ethyl alcohol which is pre-eminently alcohol in ordinary usage. This and neighbouring members of the series result from the fermentation of fruit juices, starch, vegetable extracts, the liquor from malt, and various sugars; the latter are present in ripe fruits and starch is chemically close to the sugars. Wines, cider, perry, and various beers are all products of fermentation, and the ethyl alcohol present is largely responsible for their distinctive characters.

Spirits are made by distillation of many fermented liquids—brandy from wine (of the grape), whisky (*usque baugh*, water of life) to the Gaelic speakers (as brandy is *eau de vie* to the French) from malt liquors, rum from molasses (a by-product of cane sugar), and gin from the juniper berry. Since the other alcohols

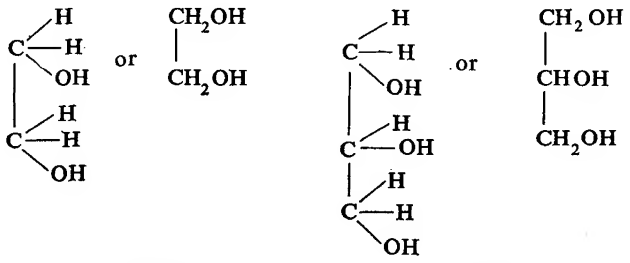
present are poisonous (many would say "so is ethyl alcohol"), their concentration during distillation makes raw spirits a danger and a process of maturing is essential. Since the maximum quantity of alcohol resulting from fermentation is from about 12 to 15 per cent, wines such as sherries and ports are fortified by the addition of brandy.

Methyl alcohol has uses as a motor-fuel, and it and some of the other lower members of the series are valuable industrial solvents. Methylated spirit is about 90 per cent ethyl and 10 per cent methyl alcohol, the latter as wood spirit, with small quantities of materials with unpleasant taste—pyridine and naphtha. Methyl violet dye is added as a means of identification. Industrial spirit is 95 per cent ethyl alcohol and 5 per cent wood spirit with no colouring matter; it is available for industrial purposes only under permit.

Since the hydroxyl radicle is present, isomerism starts with the third member of the series, and many more are possible with the higher members than is the case with the paraffins. The same type of unsaturation also occurs.

Polyhydric alcohols. Many alcohols are known with more than one hydroxyl group. The best known of these are (a) glycol or ethylene glycol which has extensive uses as a solvent and as an anti-freeze additive to water-cooled car engines, and (b) glycerol or glycerine, also a useful solvent but used principally in the preparation of nitro-glycerine and other explosives. Glycerol has many therapeutic applications.

The graphic formulae of these compounds are:



Glycol Glycerol

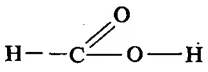
In the explosive the H of the hydroxyl is replaced in each position by the nitrate radicle $-NO_3$; its correct name is glyceryl trinitrate; this is a very dangerous material, but if it is absorbed in inert substances such as *kieselguhr* (an earthy siliceous powder) as dynamite (Nobel, 1867) or in sawdust and woodpulp, it may be handled safely.

The aliphatic or fatty acid series. (C_nH_{2n+1} COOH). (Table 13.7). The carboxyl group — COOH is characteristic of organic acids. It should be noted that while many hydrogen atoms may be present, that which confers the acid properties is the final hydrogen which terminates, in the conventional formulae, the carboxyl group.

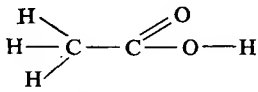
The first member of the series is formic acid, HCOOH, which does not conform to the general formula. Its name is derived from the Latin for ants (*formica*) which secrete this acid and discharge it at an enemy. The stinging nettle also contains small quantities in its hair-like spines.

The second member is acetic acid, CH_3COOH, and this is by far the most important of the organic acids. It gives the characteristic quality to vinegar in which it is dissolved to about 5 per cent; it was, indeed, the earliest known acid, and its name and that of its most obvious property is derived from the Latin *acere* (*acidus*) meaning 'sour'. Concentrated acetic acid freezes at room temperature or just below and it is consequently described as glacial.

The structure of these acids is probably



Formic acid



Acetic acid

It will be observed from study of the above formulae that these acids may be considered as paraffins in which a hydrogen atom has been replaced by the carboxyl group (COOH) and, as is to be expected, there are isomeric and unsaturated varieties of the normal form.

TABLE 13.7. SOME ALIPHATIC OR FATTY ACIDS

Molecular formula	Acid	Molecular formula	Acid
$HCOOH$	Formic	$C_{11}H_{23}COOH$	Lauric
CH_3COOH	Acetic	$C_{13}H_{27}COOH$	Myristic
C_2H_5COOH	Propionic	$C_{15}H_{31}COOH$	Palmitic
C_3H_7COOH	Butyric	$C_{17}H_{35}COOH$	Stearic
C_4H_9COOH	Valeric		

Esters. These are compounds with some analogies to inorganic salts. The reaction between acetic acid and ethyl alcohol gives ethyl acetate, that is, the ethyl ester of the acid and water:

$$\begin{matrix} CH_3\,COO\boxed{H} \\ + \\ C_2H_5\boxed{OH} \end{matrix} \longrightarrow CH_3\,COOC_2H_5 + H_2O$$

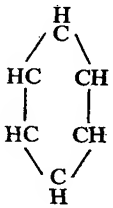
An ester is defined as a compound derived from the reaction of an organic (sometimes an inorganic) acid and an organic group, usually an alcohol. The esters of the lower organic acids and the alcohols, the greater number of which may be synthesized, contribute the agreeable flavours and odours to fruit and flowers, fats and oils are the esters of glycerol and the higher acids—hence fatty acids. These oils of vegetable origin—olive, palm, coconut, and very many others—are quite distinct from the oils of the paraffin series used as lubricants and as fuels.

CYCLIC COMPOUNDS

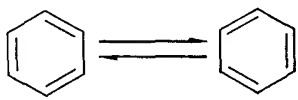
Introduction. The importance of the tetravalency of carbon must again be stressed; the existence of so many unsaturated compounds is not contrary to the principle, since, as has been shown, unsaturation confers great chemical activity and thus the saturated state is readily achieved.

Benzene was discovered by Faraday in 1825 but its formula remained in doubt until it was established as C_6H_6, largely as a result of the work of A. W. Hofmann (1818–92). However, this formula suggests a highly unsaturated (or even an impossible) substance, but benzene resembles the paraffins in many of its properties—it is stable and most of its derivatives are substitution products. Suggestions were advanced and discarded and the solution came from F. A. Kekulé (1829–96); it ranks among the great discoveries in chemistry and, indeed, in all science. Kekulé has recorded that, while working on a textbook, he dozed in front of his fire and had a vision of 'whirling snakes' which seized their own tails. The conception of the ring of six carbon atoms was born: the hypothesis appeared in 1866.

The structure of benzene. The original view of the structure was that it was a closed ring of six carbon atoms each with an attached hydrogen:



This, however, is incomplete since it does not exhibit tetravalent carbon atoms to satisfy the apparent saturation of the compound. Kekulé overcame this difficulty by suggesting alternating or oscillating double bonds; in the following diagram the benzene molecule is shown by the hexagon only:



The opposed arrows are intended to signify the dynamic equilibrium of the molecule. It is therefore held that the rapid oscillation achieves the virtual condition of saturation and, although it may appear somewhat unconvincing at first sight, the hypothesis

remains unshaken to this day while the hexagon itself, with or without the double bonds, has been called "the best-known symbol in all science".

Benzene. The chief source of benzene—also known as benzol and benzole—is coal tar. 1000 kg of the tar yields about 16 kg of benzene together with several of its derivatives and related substances. It also occurs in some petroleums again with a number of derivatives.

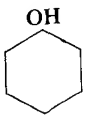
Benzene is the simplest example of a homocyclic or carbocyclic compound, i.e. its ring is composed of carbon atoms only.

BENZENE DERIVATIVES

Introduction. It has been stated that three-quarters of organic chemistry is devoted to the derivatives of benzene; together these are the aromatic compounds—the adjective because many of the earliest derivatives were fragrant and, indeed, there are those who hold that benzene itself has that quality. The vast majority of natural organic substances are aliphatic while the benzene derivatives are almost wholly synthetic.

It is evident that it is possible here to deal only with a few of this host of examples.

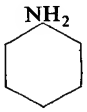
Some monosubstituted benzenes. It is usual, in the interest of brevity, to set down the substitution products of benzene in the form of the hexagon with the substituents attached. Although the conventional figure is elongated vertically, it is strictly a regular hexagon, and a single substituent may be placed at any of the vertices but, again conventionally, it is commonly shown at the top.



hydroxybenzene

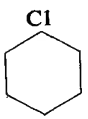
phenol

carbolic acid

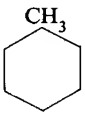


aminobenzene

aniline

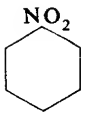


chlorobenzene

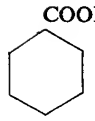


methylbenzene

toluene

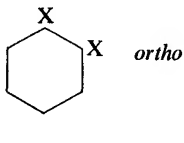


nitrobenzene



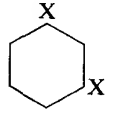
benzoic acid

Some disubstituted benzenes. There are six points on the benzene nucleus at which substitution may occur and thus, given two substituents, inspection will confirm that there are three possible arrangements, indicated in the formula by the prefixes ortho, meta, and para—usually shown by the initial letters.



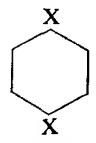
ortho

Adjacent points



meta

Separated one point

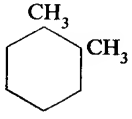


para

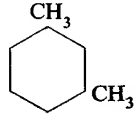
Opposed points

The compounds given below are examples of a type of isomerism in which, as in the paraffins, the isomers differ in physical and some chemical properties in spite of the close relationship in structure and composition:

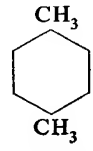
Dimethylbenzenes. Xylenes



o–Xylene

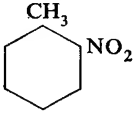


m–Xylene

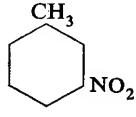


p–Xylene

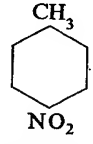
Nitrotoluenes



o–Nitrotoluene



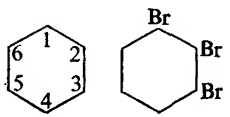
m–Nitrotoluene



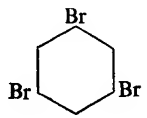
p–Nitrotoluene

The majority of photographic developing agents are benzene derivatives, principally disubstituted compounds; they are considered in the chapter on the chemistry of photography.

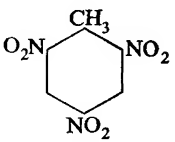
Some polysubstituted benzenes. With more than two substituents the simplest method of indicating orientation is by numbering the points of substitution but compounds are frequently named as secondary derivatives:



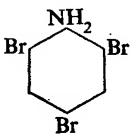
1,3,5: Tribromobenzene



1,3,5 (or symmetrical): Tribromobenzene

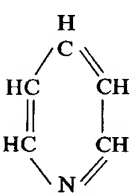


2,4,6: Trinitrotoluene (TNT) (high explosive)

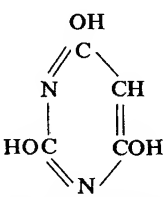


2,4,6: Tribromoaniline

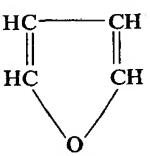
Heterocyclic compounds. The substances with a ring structure in their molecules in which atoms of more than one element take part are known as heterocyclic. Carbon is almost invariably dominant and the other components are confined to nitrogen, oxygen, and sulphur with rare exceptions, the first named being of the greatest importance:



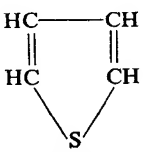
Pyridine



Barbituric acid



Furan



Thiophene

Pyridine occurs in coal tar; its molecule consists of one nitrogen atom associated with five carbon atoms to form the six-membered ring. It is a colourless liquid with an objectionable smell (some say fishy). Pyridine is added to methylated spirit to make it unpalatable (see under alcohol above); its derivatives are important in medicine.

Barbituric acid is the root of the barbiturates many of which are drugs with sedative or soporific properties. The ring contains two nitrogen with four carbon atoms.

Furan is a colourless liquid which occurs in some wood tars. Its molecule has a five-membered ring of one oxygen with four carbon atoms.

Thiophene is structurally very similar to furan, the oxygen atom of the latter being replaced by sulphur. It occurs in small quantities in coal tar associated with benzene.

These four compounds may be accepted as typical of a very large class of organic substances. All of them are more important in their derivatives than in their original form.

Polymerization. When acetylene is passed through a metal tube raised to a low, red heat in the absence of oxygen, a small quantity of benzene is produced:

$$3\,(C_2H_2) \longrightarrow C_6H_6$$

This may be considered a simple example of addition polymerization which is defined as the union of several molecules of the same compound to form another substance of the same empirical composition but which differs in molecular weight and may differ in chemical and physical properties.

Many important plastics are the result of this type of polymerization:

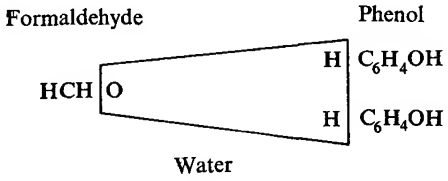
$(H_2C = CH_2)_n$	$(H_2C = CHOH)_n$
Polyethylene "polythene"	Polyvinyl alcohol "PVA"

Polythene is a tough flexible material with electrical insulating properties; its most familiar form is as translucent sheet of many uses. PVA is the base of many photoresists in reproduction

processes; it has tended to displace some of the standard natural substances and it is further discussed in Chapter 19 on these processes.

It should be noted that the units of these polymers are unsaturated. It is, indeed, this condition which promotes the formation of these giant molecules, giant since the whole sheet or fabricated article may well be a single molecule. (The polyvinyl unit is strictly the vinyl radicle $H_2C = CH—$; vinyl alcohol itself is probably hypothetical.)

The other principal type is condensation polymerization in which molecules of different compounds coalesce usually with elimination of part of the components:



The actual polymerization is promoted by heat in the presence of activating agents, usually metallic oxides; the result is phenol-formaldehyde which, while among the earliest, remains one of the best known of the plastics.

Polymerization is very important in the setting of printing inks; it is consequently further considered in Chapter 21.

The classification of plastics given above as addition or condensation polymers is almost wholly chemical. There is a further classification in which these materials are distinguished by their physical properties as (a) thermoplastic—i.e., they may be softened or even melted by heat and remoulded the process being repeatable, and (b) thermosetting—in which the process is irreversible, i.e. when the plastic has been shaped by pressure and heat it cannot be further changed.

EXPLANATORY NOTES TO APPENDICES (pp. 240–3)

AN Atomic number
AW Atomic weight.
SG Specific gravity: where allotropes exist, that of the most common is given.

Chief sources. Where there are several of equal importance the most familiar is given.

Extraction

(a) *Electrolysis.* Usually the passage of current through fused compound.
(b) *Thermal.* Reduction by heat, sometimes in presence of reducing agent, i.e. carbon with iron ores.
(c) *Thermal* (*Goldschmidt*). The metallic oxide and aluminium powder ignited in crucible; these metals rarely needed in elemental form.
(d) *Distillation.* Fractional, i.e. of liquid air or, in some cases, cadmium, zinc, with selective sublimation.
(e) *Reduction* (*chemical*). Displacement from compound by substance of greater activity, i.e. iodine from iodide by chlorine.

Valencies. The most common are shown; where almost every possible valency occurs, i.e. phosphorus, this is given as 'varied' or, where almost inactive, not indicated, i.e. helium.

APPENDIX A

BRIEF INFORMATION ON FAMILIAR ELEMENTS IN ALPHABETICAL ORDER

Element	Symbol	AN	AW	SG	Chief sources	Extraction	Valencies
Aluminium	Al	13	27	2·7	Bauxite (Al_2O_3)	Electrolysis	3
Antimony	Sb	51	121·7	6·6	Stibnite (Sb_2S_3)	Thermal	3,5
Barium	Ba	56	137·3	3·8	Barytes ($BaSO_4$)	Electrolysis	2
Bismuth	Bi	83	209	9·8	Bismuth glance (Bi_2S_3)	Thermal	3
Bromine	Br	34	79·9	3·12	Bromides (X Br)	Displacement by chlorine	1
Cadmium	Cd	48	112·4	8·65	In zinc ores	Distillation	2
Calcium	Ca	20	40·1	1·53	Limestone ($CaCO_3$) Chalk	Electrolysis of fused $CaCl_2$	2
Carbon	C	6	12	2·3	Free. Graphite	———	4
Chlorine	Cl	17	35·5	Gas	Common salt (NaCl)	Electrolysis	1
Chromium	Cr	24	52·0	7·1	Chromite ($FeCr_2O_4$)	Thermal (Goldschmidt)	2,3
Cobalt	Co	27	58·9	8·8	Smaltite ($CoAs_2$)	Thermal	2
Copper	Cu	29	63·5	8·95	Free. Cuprite (Cu_2O) Copper glance (Cu_2S)	Thermal Electrodeposition	1,2
Gold	Au	79	197·0	19·4	Free	———	1,3
Helium	He	2	4	gas	Hot springs Natural gas	———	———
Hydrogen	H	1	1	gas	Water (H_2O)	Electrolysis	1
Iodine	I	53	127·0	4·9	Iodides (XI)	Chemical reduction	1
Iron	Fe	26	55·8	7·9	Haematite (Fe_2O_3)	Thermal	2,3
Lead	Pb	82	207·2	11·3	Galena (PbS)	Thermal	2,4
Magnesium	Mg	12	24·3	1·74	Magnesite ($MgCO_3$)	Electrolysis	2

Manganese	Mn	25	54·9	7·06	Pyrolusite (MnO_2)	Thermal (Goldschmidt)	1,2,3
Mercury	Hg	80	200·6	13·6	Cinnabar (HgS)	Thermal	1,2
Nickel	Ni	28	58·7	8·9	Pentlandite ($NiFe_2S_3$)	Thermal	2
Nitrogen	N	7	14·0	Gas	Atmosphere	Distillation of liquid air	Varied
Oxygen	O	8	16·0	Gas	Atmosphere	Distillation of liquid air	2
Phosphorus	P	15	31·0	1·8	Phosphorite ($Ca_3(PO_4)_2$)	Thermal	Varied
Potassium	K	19	39·1	0·85	Sylvine (KCl)	Electrolysis	1
Selenium	Se	34	79·0	4·5	Selenides (MSe_x)	Chemical reduction	4
Silicon	Si	14	28·1	0·85	Silica (SiO_2)	Thermal (Goldschmidt)	4
Silver	Ag	47	107·8	10·5	Argentite (Ag_2S)	Cyanide process	1
Sodium	Na	11	23·0	0·97	Common salt (NaCl)	Electrolysis	1
Sulphur	S	16	32·0	2·0	Free	Pumped from deposits (Frasch process)	2
Tin	Sn	50	118·7	7·2	Cassiterite (SnO_2)	Thermal	2,4
Titanium	Ti	22	47·9	4·5	Rutile (TiO_2)	Thermal (Goldschmidt)	2,3,4
Tungsten	W	74	183·8	19·0	Wolframite ($FeMnWO_4$)	Chemical reduction	3
Uranium	U	92	238·0	18·7	Pitchblende (U_3O_8)	Processes of reduction	Varied
Zinc	Zn	30	65·3	7·1	Zinc blende (ZnS)	Thermal and sublimation	2

Appendix B

Table of the Elements in Order of Atomic Number

AN	Name	Symbol	AW	AN	Name	Symbol	AW
1	Hydrogen	H	1·0	53	Iodine	I	127·0
2	Helium	He	4·0	54	Xenon	Xe	131·3
3	Lithium	Li	7·0	55	Caesium	Cs	133·0
4	Beryllium	Be	9·0	56	Barium	Ba	137·3
5	Boron	B	11·0	57	Lanthanum	La	139·0
6	Carbon	C	12·0	58	Cerium	Ce	140·0
7	Nitrogen	N	14·0	59	Praseodymium	Pr	141·0
8	Oxygen	O	16·0	60	Neodymium	Nd	144·3
9	Fluorine	F	19·0	61	Promethium	Pm	—
10	Neon	Ne	20·0	62	Samarium	Sm	150·3
11	Sodium	Na	23·0	63	Europium	Eu	152·0
12	Magnesium	Mg	24·3	64	Gadolinium	Gd	157·2
13	Aluminium	Al	27·0	65	Terbium	Tb	159·0
14	Silicon	Si	28·1	66	Dysprosium	Dy	162·5
15	Phosphorus	P	31·0	67	Holmium	Ho	165·0
16	Sulphur	S	32·0	68	Erbium	Er	167·3
17	Chlorine	Cl	35·5	69	Thulium	Tm	169·0
18	Argon	Ar	39·9	70	Ytterbium	Yb	173·0
19	Potassium	K	39·1	71	Lutetium	Lu	175·0
20	Calcium	Ca	40·1	72	Hafnium	Hf	178·5
21	Scandium	Sc	44·9	73	Tantalum	Ta	181·0
22	Titanium	Ti	47·9	74	Tungsten	W	183·8
23	Vanadium	V	51·0	75	Rhenium	Re	186·2

24	Chromium	Cr	52·0
25	Manganese	Mn	54·9
26	Iron	Fe	55·8
27	Cobalt	Co	58·9
28	Nickel	Ni	58·7
29	Copper	Cu	63·5
30	Zinc	Zn	65·3
31	Gallium	Ga	69·7
32	Germanium	Ge	72·6
33	Arsenic	As	74·9
34	Selenium	Se	79·0
35	Bromine	Br	79·9
36	Krypton	Kr	83·8
37	Rubidium	Rb	85·4
38	Strontium	Sr	87·6
39	Yttrium	Y	89·0
40	Zirconium	Zr	91·2
41	Niobium	Nb	92·9
42	Molybdenum	Mo	96·0
43	Technetium	Tc	——
44	Ruthenium	Ru	102·0
45	Rhodium	Rh	103·0
46	Palladium	Pd	106·4
47	Silver	Ag	107·8
48	Cadmium	Cd	112·4
49	Indium	In	114·8
50	Tin	Sn	118·7
51	Antimony	Sb	121·7
52	Tellurium	Te	127·6

76	Osmium	Os	190·2
77	Iridium	Ir	192·2
78	Platinum	Pt	195·0
79	Gold	Au	197·0
80	Mercury	Hg	200·6
81	Thallium	Tl	204·4
82	Lead	Pb	207·2
83	Bismuth	Bi	209·0
84	Polonium	Po	—
85	Astatine	At	—
86	Radon	Rn	—
87	Francium	Fr	—
88	Radium	Ra	—
89	*Actinium*	Ac	—
90	Thorium	Th	232·0
91	Protoactinium	Pa	—
92	Uranium	U	238·0
93	Neptunium	Np	—
94	Plutonium	Pu	—
95	Americium	Am	—
96	Curium	Cm	—
97	Berkelium	Bk	—
98	Californium	Cf	—
99	Einsteinium	Es	—
100	Fermium	Fm	—
101	Mendelevium	Md	—
102	Nobelium	No	—
103	Lawrencium	Lw	—

Part IV

Applied Chemistry

CHAPTER 14

Elementary Photographic Chemistry

Introduction. Photography is both a physical and a chemical process. It is physical since an optical system is necessary to direct light in such a manner that an image falls on the light-sensitive material. This aspect is considered in Chapter 9 on light and optics. There can, however, be no doubt that the greater part of the practice of photography is applied chemistry. The matter which follows is concerned with the subject in its normal if most restricted sense—that which involves various salts of silver.

Silver halides and the visible image. All silver salts display instability in varying degrees; some are readily decomposed by the action of light.

When silver chloride is prepared by the reaction between silver nitrate and a soluble chloride or dilute hydrochloric acid, the precipitate is quickly blackened on exposure to bright light:

$$AgNO_3 + NaCl \longrightarrow NaNO_3 + AgCl \downarrow$$

(the downward arrow indicates precipitation)

$$2AgCl \xrightarrow{\text{light}} 2Ag + Cl_2$$

The blackening is evidently due to the liberation of silver in some form; it is, in fact, possible to show that it is the metal in a state of fine division.

This phenomenon was known to the later alchemists, but the explanation was not known until the eighteenth century.

The great Swedish chemist, C. W. Scheele (1742–86) is regarded as the founder of the photochemistry of the silver salts, and among his discoveries is the decomposition of the chloride of silver by light as set down in modern terms above.

The other silver halides may be prepared in the same manner as the chloride, but the visible action of light is slower on silver bromide and very much slower on silver iodide. It should be observed that silver fluoride stands apart; it has considerable aqueous solubility and is not apparently decomposed by light.

Most of the earlier experimenters in this field used paper impregnated with silver chloride to obtain prints of leaves and other small, flat objects, but, since they were unable to remove the unexposed salts, the images were lost.

The first photograph? The earliest known (1826) permanent image produced by light through a lens was that by N. Niepce (1765–1833). A pewter plate coated with a thin layer of bitumen was given an exposure of 8 or 9 hours to a scene in the bright sunlight of the south of France; the unexposed bitumen was removed by a solvent leaving an image in insolubilized bitumen on the whitish metal. In France, Niepce is considered to be the inventor of photography, but since the process was incapable of further development this claim is not generally accepted. However, Niepce used the same method 2 years before to make what is undoubtedly the first photoengraving. A metal plate, probably copper, was bitumen-coated and exposed in contact with an engraving; the unexposed bitumen was removed and the plate etched. Impressions, some of which are extant, were made from the intaglio plate on a copperplate press.

Daguerreotype. J. M. Daguerre (1787–1851) was the inventor of the beautiful process which bears his name. A polished silver or silvered copper plate was subjected to iodine vapour, and thus a layer of light-sensitive silver iodide was formed on the surface. After a rather prolonged exposure in a camera the plate was developed by mercury vapour during which the mercury was deposited on the unexposed areas; the silver iodide was removed in

a concentrated solution of common salt (later in hypo). The process rapidly became popular everywhere and it remained in use long after more effective methods became available, especially in the United States. Examples of daguerreotype may be seen in many museums and private collections.

Fox Talbot. Elegant though it was, the weakness of daguerreotype was that it is a direct positive process and, in consequence, every photograph on its metal plate is an individual creation. The first negative–positive process of photography was disclosed to the Royal Society in a paper read by the inventor, William Henry Fox Talbot (1800–77) on 31 January 1839. Fox Talbot was aware that disclosure of daguerreotype was imminent (it was made known on 18 August 1839) and he rather unchivalrously got in first.

For all that, almost all historians ascribe the invention of photography to Fox Talbot; there is, indeed, no doubt whatever that photography in the modern sense of a negative–positive process using silver salts has grown from the seedling of 1839.

In the Calotype process—the name was first used in 1841—paper is impregnated with silver iodide (the actual method is a little in dispute); after exposure, gallic acid with some silver nitrate is used as a developer. This was therefore the first successful instance of development of the latent image (see below), and consequently exposures were enormously reduced. Some of the work produced by Fox Talbot's Calotype, particularly that of Julia Margaret Cameron and David Octavius Hill, is ranked among the finest in all photography.

The wet-collodion process. The first really efficient negative process on glass was published in 1851 by F. Scott Archer (1818–1857). In this process, collodion containing alcohol soluble iodides with some bromides is bathed in silver nitrate, and thus light-sensitive silver halides are produced in the collodion on its glass support. The plate is exposed, still wet, and developed at once. This again, is an example of development of the latent image.

The wet-collodion process became extremely popular; it was used to photograph aspects of the Crimean War and wet-plate photographers were sent by the United States Government to

record the Indians of the Great Plains as they were before civilization caught up with them.

However, in the present context, the process is important because it was used almost exclusively for monochrome line and halftone photography until quite recently. While wet-collodion survives here and there, it appears likely that it will eventually die: dry plates and films are much more easily handled and processed. It is all but certain that this has the longest record of continuous use in the history of photography.

Gelatin emulsions. So many investigators took part in the search for a method of preparing and supporting the silver halides in gelatin that it is almost an embarrassment to use names, but by 1879 the manufacture of dry plates was commercially important in much of western Europe and in the United States.

'Emulsion' has been used from the early days of the dry plate, but the sensitive coating is strictly a suspension of silver halide in the gelatin; an emulsion is a dispersion of one liquid in another in which it is not normally miscible as, for example, minute droplets of oil in water.

Protective action of gelatin. When a silver halide is formed in water as in the equation above it tends to flocculate into clusters which almost prevent ordinary filtration by clogging the filter paper; but when it is formed in gelatin by the same method, flocculation is largely inhibited and the halide is dispersed as small granular or crystalline aggregates. This property of gelatin is very important for photography.

Emulsion manufacture. A carefully controlled solution of silver nitrate is added to alkali halides contained in aqueous gelatin. Silver bromide is the principal sensitive salt but the iodide is often present and, more rarely, the chloride. A process called ripening follows—largely subjection to heat—during which the character of the emulsion is formed. In general terms the coarse-grained products have high sensitivity while fine-grained emulsions are less sensitive and give the higher contrast needed for process photography in line and halftone. The soluble products of the action are removed by washing for most purposes but are allowed to remain for many printing papers.

Speed of emulsions. Silver bromide in pure gelatin has a relatively low sensitivity, but many emulsions are available which are effective with extraordinarily brief exposures. It has been shown that the raw gelatin contains very small quantities of organic sulphur compounds which, during the manufacturing process, assist in the formation of microscopic specks of silver sulphide on the silver halide crystals; strains result in the structures of the latter which promote or accelerate the formation of the latent image upon the impact of light (see below).

The latent image. The visible image given by the silver halides after more or less prolonged exposure has been considered above. However, no image whatever is apparent with the very short exposures normal with dry emulsions, but it is evident that the light has had some effect since an image appears on development. It is now established that the latent image consists of small particles of metallic silver which constitute nuclei around which development occurs. The silver sulphide induced stresses contribute to the action.

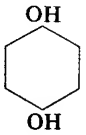
DEVELOPMENT

Introduction. The difference between the visible and latent images is clearly quantitative only; the function of development is to reduce to metallic silver all the exposed silver halide around the latent image.

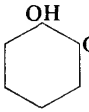
Photographic development is conventionally divided into two types: (a) Physical, in which the silver is reduced from free silver nitrate on the surface of the emulsion; in its most complete form this is encountered in the wet-collodion process; it is also partly in evidence in Fox Talbot's Calotype. (b) Chemical, in which the exposed silver halide itself is reduced to silver; this may be said to be normal development.

In fact, in other than the subtle distinction stated, all photographic development is chemical; it is probable that in all development both types occur but the physical aspect is very slight normally; where an image as free from grain as possible is required developing solutions are prepared with considerable physical activity.

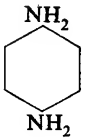
Developing agents. A developing agent is that part of the developer which actually reduces the silver salts; the great majority are di-substituted or tri-substituted benzene derivatives. The common substituents are hydroxy (-OH) and amino ($-NH_2$) groups. In the di-substituted compounds the substituents must be in the ortho or para positions; those in the meta positions and the symmetrical (2, 4, 6) tri-substituted benzenes are not developing agents. Among the agents in common use are:



hydroquinone
quinol

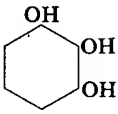


pyrocatechol
pyrocatechin

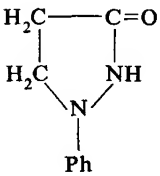


paraphenylene – diamine

metol



pyrogallol
pyro

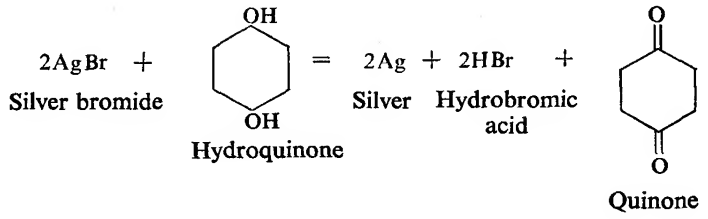


'Phenidone' (Ilford)

Function of the developing agent. The reactions of development are (a) the reduction of the exposed silver halide to metallic silver, and (b) the simultaneous oxidation of the developing agent by the removal of oxygen (see Chapter 11, under 'Oxidation and reduction', p. 188).

Hydroquinone has probably been studied more than any other

developing agent; its action may be represented in the simplest possible manner as:



or, in the abbreviated form,

$$2AgBr + C_6H_4(OH)_2 = 2Ag + 2HBr + C_6H_4O_2$$

The developer solution. The developing agent cannot function in isolation—several other components are necessary:

(a) *The accelerator.* The accelerators in ordinary use are the alkali carbonates and hydroxides; other materials enter into the developer for unusual purposes: these may include formaldehyde, ammonia, borates and trisodium phosphate. Among the products of development is hydrobromic acid, and the most obvious explanation of the need for an alkaline compound is the presence of this acid which would inhibit the action completely if allowed to remain:

$$HBr + NaOH = NaBr + H_2O$$
$$(\text{acid} + \text{base} = \text{salt} + \text{water again})$$

This is to state that the developer must be alkaline, i.e. that the pH of the solution should be above pH 7.

(b) *The preservative.* In alkaline solution the developing agents are subject to oxidation from the air and from some of the intermediate products of development. A preservative or antioxidant —sodium sulphite or bisulphite or potassium metabisulphite are widely employed—is added to the solution.

(c) *The restrainer.* In the passage on the accelerator above sodium bromide is shown among the products; this compound is completely ionized in solution:

$$NaBr \xrightarrow{\text{water}} Na^+ + Br^-$$

The addition of any substance which ionizes in the same manner represses the formation of the bromide and thus of the reduction of the silver bromide to silver. Therefore the presence of potassium bromide in small amount restrains the action and prevents the appearance of general fog.

(d) *Water.* This is the normal solvent for this and a vast range of other purposes. Ideally, water for the developer should be distilled but it is usually ruled out by the cost. Most tap-waters may be used but very hard supplies should be treated by one or other of the commercial softeners.

The fixing solution. The exposed and developed emulsion is fixed by the action of sodium thiosulphate which removes the residual silver bromide. This action is very complex; in its most simple form it may be shown as:

$AgBr$	$+$	$3Na_2S_2O_3$	$=$	$NaBr$	$+$	$Na_5Ag(S_2O_3)_3$
Silver bromide		Sodium thiosulphate		Sodium bromide		Sodium argento-thiosulphate

but a whole series of sodium argentothiosulphates are probable since that shown above has low solubility.

The plate is often transferred to the fixing bath with an appreciable quantity of the developing agent still present; this may result in staining since development would continue during fixation. This staining is very usually prevented by the addition to the fixing bath of small quantities of acid or of a salt which is acid in solution to destroy the developing agent. Sodium (or potassium) metabisulphite is most commonly in use; sulphurous acid occurs in solution:

$Na_2S_2O_5$	$+$	H_2O	$=$	Na_2SO_3	$+$	H_2SO_3
Sodium metabisulphite		Water		Sodium sulphite		Sulphurous acid

The addition of dilute acetic acid and sodium sulphite to the fixer also gives sulphurous acid.

Fast fixation. The substitution of ammonium thiosulphate for the sodium salt accelerates fixation since the ammonium radicle also has solvent properties on the silver halide. Proprietary materials are available which act in this manner.

Reduction. It is frequently desirable to decrease the silver density—this applies particularly in process photography. Farmer's reducer is in almost unchallenged use for the purpose; it consists of a mixture of ferricyanide and hypo and some control is possible by varying the quantities of each component. However, it is more convenient to consider the action in two parts:

(a) $4Ag + 4K_3Fe(CN)_6 = Ag_4Fe(CN)_6 + 3K_4Fe(CN)_6$

Silver — Potassium ferricyanide — Silver ferrocyanide — Potassium ferrocyanide

(b) $Ag_4Fe(CN)_6 + 4Na_2S_2O_3 = 4NaAgS_2O_3 + Na_4Fe(CN)_6$

Silver ferrocyanide — Sodium thiosulphate — Sodium argento-thiosulphate — Sodium ferrocyanide

It should be noted that photographic reduction is actually oxidation in the chemical sense.

Intensification. The aim in line and halftone photography is to obtain negatives of the maximum contrast. It is consequently sometimes necessary, after reduction or otherwise, to add to image density. While there are many methods, intensification with mercury salts is the most useful; here, again, the action is aptly shown in two stages:

(a) $Ag + HgCl_2 = AgHgCl_2$

Silver — Mercuric chloride — Silver mercurous chloride

The bleached image is blacked by a non-staining developer:

(b) $AgHgCl_2 + C_6H_4(OH)_2 = AgHg + C_6H_4O_2$

Silver mercurous chloride — Hydroquinone — Silver and mercury — Quinone

The action shown in (b) is that of development. Ammonia may be used for this blackening with some caution since it often has some reducing effect.

Sensitivity to colour. While light has been used above, the most active radiation for photographic purposes is ultraviolet and most ordinary emulsions are sensitive only to ultraviolet, and to the extreme shorter wave visible light, i.e. to blue. Active radiation in the photographic sense is that which is absorbed. Therefore if the plate is treated with a magenta (blue–red) dye, the green element of white light is absorbed and green sensitivity given to the emulsion. Such sensitivity is called orthochromatic. A panchromatic emulsion is also sensitive to red, and to procure this type of sensitivity the emulsion must be bathed in dyes which between them absorb the whole of the visible spectrum (see Chapter 10, on Colour). The above states the complex subject in what is certainly an over-simplified manner, and students are referred to one or other of the many excellent books which deal with the science of photography.

The pH of developers. A brief reference is made above under the heading "The developer solution" to this subject. In principle all developing agents have an optimum pH value, i.e. a usually alkaline condition in which they function most effectively. It has, indeed, been asserted that the development rate for any developing agent is very largely related to the pH value of the solution in which they are used.

Hydroquinone, the most widely employed developing agent in line and halftone photography, is almost inactive at pH values much below pH 8, particularly if the developer is cold, and it performs at its best at pH 9.

In the earlier days of photography the compilation of developer formulae was rather a matter of trial and error; today a formula is prepared with the pH aspects of all the components and their interaction fully in view.

CHAPTER 15

Metals of Printing Surfaces

Introduction. The image-bearing metals are very conveniently divided into two clearly defined groups:

(a) The metals used for casting as type, mechanical composition, stereotyping, and electrotype backing; it is obvious that this group is confined to letterpress printing.

(b) The metals used for line and halftone photoengraving, photolithography, and photogravure; these metals are etched into relief for letterpress and the converse for intaglio (cut-in); they provide plates for surface photolithography in which the difference between image and non-image is determined solely by the selective character imparted to the metal and for deep-etch plates in which the image areas are etched below the general level but in which there is no fundamental distinction to surface plates since, almost invariably, the recesses are filled in with an impervious material.

(a) CASTING METALS

Alloys. Metals are not often used in the pure state, and for most industrial purposes alloys are favoured.

The simple statement that an alloy consists of two or more metals is hardly adequate as a definition since it suggests nothing about the manner in which the components are united. The

majority of alloys are solid solutions, a few may be regarded as mere mixtures, while some very important alloys consist in part of compounds of the dominant metal with another element together with some other metal or metals. Thus steels contain compounds of iron and carbon of the type Fe_3C; other metals—manganese chromium—and even non-metals—silicon—are added according to purpose.

An alloy may share in some manner the properties of its constituents, but frequently an alloy gives evidence of unexpected qualities which make it of greater value.

As is to be supposed, the metallurgy of iron and its alloys has been studied more than that of any other metal. Wrought-iron is closest to the pure metal; it is relatively soft and freely malleable and it therefore has many uses where easy fabrication is the main criterion; mild steel has a low carbon content and it may be fabricated with little more difficulty than wrought iron. High carbon steels give the hard alloys for cutting tools while chromium-steel furnishes the stainless alloy of cutlery in which the cutting edge is less important although its qualities in this respect have been very much improved in recent years.

Cast-iron is the least determinate alloy of the metal—it has considerable content of the iron–carbon compound together with variable quantities of sulphur, silicon, phosphorus, and perhaps manganese. It has great rigidity and is used consequently for the bed plates of machines and, since it is almost inert chemically, it is used to provide containers for acids and other corrosive materials.

Movable type. The first type faces were engraved on wood but, since the casting of soft metals in moulds was already practised, metal type must have been in use quite early in the history of the art and craft. The earliest reference to type casting in metal appeared in 1540, the alloy being the expensive pewter (about 4 parts tin to 1 part lead). Lead itself is far too soft to be really effective, and it was quickly discovered that the addition of the then uncertainly known antimony not only gave much better quality of cast but it could replace some of the valuable tin.

Lead, antimony, and tin remain the constituents of printing

alloys for casting; a very small amount of copper is added for some purposes.

The Alloy Metals

Some information on the elements appears in Appendix A of Part III, it is proposed to briefly augment this material.

Lead. This metal has been known almost from the beginning of history largely because it is easily extracted from its ores and because of the ease of fabrication. The principal source is galena (lead sulphide); other ores are cerussite (carbonate) and anglesite (sulphate).

Extraction. The galena is heated in a furnace to the molten state; during the heating there are a number of intermediate reactions including the oxidation of the sulphide, but the overall process may be represented simply as

$$PbS + O_2 = Pb + SO_2$$

Lead sulphide — Oxygen (from air) — Lead — Sulphur dioxide

The sulphur dioxide is largely used in the manufacture of sulphuric acid.

The lead as extracted contains many impurities, chiefly antimony, arsenic, zinc, and silver. Other than the last named, these are removed by remelting the lead in ample hot air when oxidation occurs to form a scum on the surface of the melt which is raked off. The silver and most of the lead are not affected by this process; the increasingly valuable silver is separated by Parke's process which, briefly, involves selective solution in zinc and by cupellation in which, again briefly, the lead–silver alloy is subjected to blasts of very hot air; the lead is oxidized to litharge (PbO) and the silver remains.

Properties. The melting point of lead is 327°C (621°F). It is a soft grey metal of high malleability and ductility. Lead and its alloys have wide industrial applications; it is of interest that the most important alloys—solders, fusible alloys, bearing metal, and even accumulator plates—use one or both of the other components of the printing metals under consideration.

As suggested above, lead alone is too soft for the present purpose and, of greater importance, it gives poor definition when cast.

Antimony. The only source of any consequence is stibnite (antimony sulphide); this black compound had, and still has in the Orient, cosmetic uses. The metal has been long known although it was often mistaken for lead.

Extraction. Two processes are employed; the older is most effective with high grade ore. Stibnite is fused with scrap iron:

$$\underset{\text{Antimony sulphide}}{Sb_2S_3} + \underset{\text{Iron}}{3Fe} = \underset{\text{Antimony}}{2Sb} + \underset{\text{Ferrous sulphide}}{3FeS}$$

The more modern practice is to roast the stibnite in air to obtain the oxide:

$$\underset{\text{Antimony sulphide}}{2Sb_2S_3} + \underset{\text{Oxygen (from air)}}{9O_2} = \underset{\text{Antimony trioxide}}{2Sb_2O_3} + \underset{\text{Sulphur dioxide}}{6SO_2}$$

The antimony trioxide is reduced by heating with good coke or charcoal:

$$\underset{\text{Antimony trioxide}}{2Sb_2O_3} + \underset{\text{Carbon}}{3C} = \underset{\text{Antimony}}{4Sb} + \underset{\text{Carbon dioxide}}{3CO_2}$$

Properties. The melting point of antimony at 631°C (1167°F) is much higher than that of lead. It is brittle and rather hard and it exists in two forms (or allotropes)—grey, the normal metallic allotrope, and yellow, in which it exhibits few metallic qualities (refer to Chapter 11). The value of antimony is in the properties it imparts to alloys, some of which are mentioned above under "Lead". In the present context it performs two functions: it hardens the printing alloy and, of at least equal importance, it expands very slightly on solidification as a pure metal; in alloys this expansion counters the considerable contraction of its companion metals to some extent and thus tends to promote sharp and clean casts.

Tin. The bronze age was the first in which a metal became important for weapons and tools. Bronze is an alloy of copper and tin, and therefore the latter must have been known from a remote

past. Tin ore was quarried in Cornwall during the Roman period and the Cassiterides (the Tin Islands), said to be around Lands End, were visited by the Phoenicians in search of this and other metals.

Almost the sole source of the increasingly expensive metal is cassiterite, found in widely distributed, if diminishing, deposits in many parts of the world, principally Malaya and Bolivia. The very heavy ore is crushed to powder and freed from earthy matter and sand by currents of water; when present, the volatile arsenic and sulphur are removed by roasting in air and the purified tinstone is reduced by heating in a furnace with the high carbon anthracite:

$$\underset{\text{Stannic oxide}}{SnO_2} + \underset{\text{Carbon}}{2C} = \underset{\text{Tin}}{Sn} + \underset{\text{Carbon monoxide}}{2CO}$$

Properties. The melting point of tin is 232°C (449°F), well below that of lead. It is a beautiful metal, very ductile and rather soft and, like antimony, it exists in several forms. The most familiar allotrope is white or β (beta) tin which on heating to 161°C becomes the γ (gamma) allotrope of different crystal structure to normal tin, while below about 16°C the metal tends to the grey powder of δ (delta) tin. Tin is a component of many valuable alloys of which bronze is the best known.

In printing metals, tin confers fluidity to the molten alloy and wear resistance to the cast.

Copper. This metal is relatively unimportant in the casting alloys while it occupies a leading position in the photographic processes; copper is therefore considered under group (b) (p. 269).

Melting (or freezing) points of pure substances. A pure substance, whether element or compound, is characterized by a sharp and definite melting point. It should be observed that melting and freezing points may be considered identical and that compounds must be stable and not subject to decomposition at the temperatures concerned.

Cooling curves of pure substances. If a pure solid substance is heated to a temperature well above its melting point and allowed to cool in uniform conditions, a temperature–time graph recording

the process provides evidence which is, at first sight, a little surprising (Fig. 15.1):

(a) The temperature falls steadily while substance is wholly liquid.

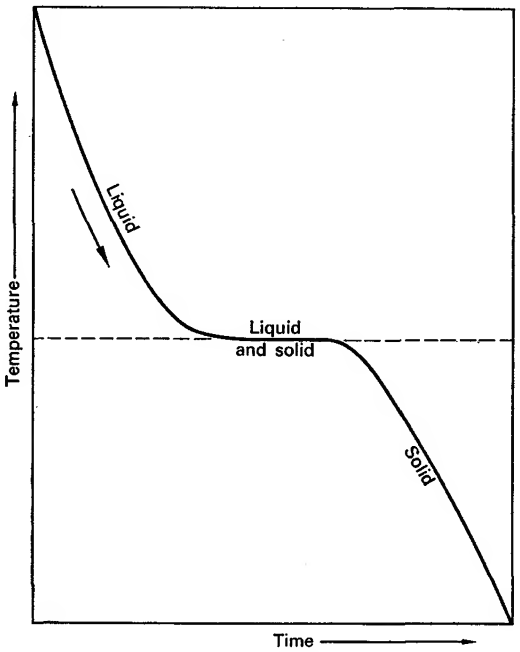


FIG. 15.1. Typical cooling curve of a pure substance.

(b) The horizontal section of the curve is at the freezing point; the temperature remains constant.
(c) During this period the heat being lost is the "latent heat of solidification".
(d) When the whole is solid, the temperature resumes its steady fall.

The metals under consideration are, as elements, "pure substances".

Cooling curve of an alloy. When an alloy or any type of solution is treated in the same manner as the pure substance above, the cooling curve (Fig. 15.2) exhibits features not apparent in the previous example:

(a) The lead starts to separate as crystals at about 265°C (509°F). There is no sharp freezing point.

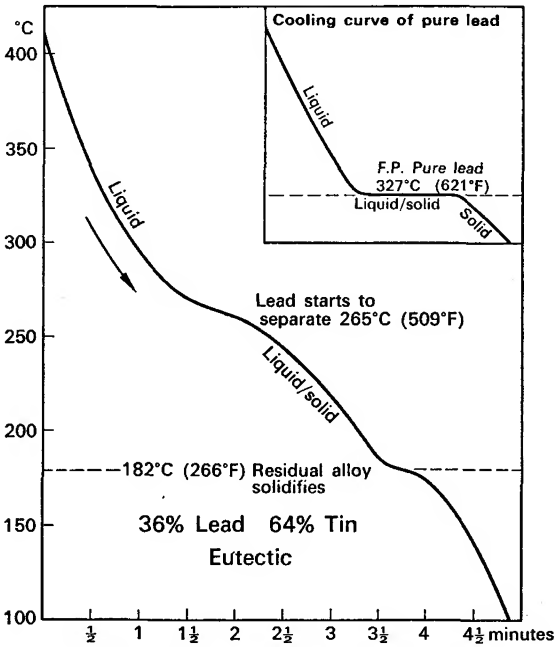


FIG. 15.2. Cooling curve of a lead-tin alloy.

(b) The separation of the lead continues to the next phase at about 182°C (266°F).

(c) The removal of the lead from the system increases the proportion of tin in the residue.

(d) At 182°C (266°F) the remainder of the alloy solidifies as a homogeneous mass with the composition 36 per cent lead

and 64 per cent tin (this is a soft solder). This temperature is at the final freezing point.

There are several matters of moment to be noted here:

(i) The indecisive freezing point is well below that of pure lead, which is 327°C (621°F).

(ii) This depression of the freezing point is characteristic of solutions as against the pure solvent; the indeterminate freezing point is typical of impure substances.

(iii) The lead is steadily removed from the alloy until the proportion of the constituents reaches, as stated, 36 per cent lead, 64 per cent tin, and the final phase is attained.

The example given is a lead-rich alloy; if a tin-rich alloy is similarly studied the tin separates first and continues until the eutectic of 36 per cent lead and 64 per cent tin is attained and the final freezing point reached. Alloys of intermediate composition adjust themselves until, again, the eutectic proportion is achieved.

There are several additional terms used to define phases in the cooling process (a) an arrest point is that region of a cooling curve where solids begin to separate; (b) the liquidus temperature that at which the alloy is just wholly liquid; (c) the solidus temperature is that at which the residual alloy enters the wholly solid state; (d) melting or freezing ranges are the temperature extremes between which solidification occurs.

The cooling process of a printing metal of three components is naturally more complex than that of the binary system considered above, and it is difficult or perhaps impossible to set down all the data without the use of a three-dimensional graph. It is, however, possible to state briefly the essential information. Three phases are evident:

(a) While the alloy continues to be a liquid the steady cooling rate is maintained.

(b) Crystalline solids separate; these are antimony, tin, or both—the actual condition is determined by the composition of the original alloy. This withdrawal of some of the constituents as solids alters the composition of the liquid remainder.

(c) The eutectic is formed by (i) tin 4 per cent, (ii) antimony 12 per cent, and (iii) lead 84 per cent; the eutectic temperature is 223°C (463°F). From this point the temperature falls steadily to that of the surroundings.

Structure of printing alloys. The alloy as cast for use may be considered as an aggregation of small antimony–tin crystals embedded in the softer matrix of the eutectic; the latter has many of the properties of a pure metal or compound.

The influence of cooling rate upon crystal size is well known in other fields; the magma, the molten material of the earth's crust, cools as it is forced towards the surface. At depth, many millions of years of incredibly slow solidification have produced the very large and beautiful crystals of quartz and feldspar of the granites, while the visually almost structureless igneous rocks of the same composition are formed by relatively rapid cooling nearer the surface. During this solidification the lighter materials tend to rise and the converse, and this action also is more marked with retarded cooling.

Printing alloys are not subject to these extremes but, nevertheless, the same influences are present. A rapid rate of cooling tends to the formation of small crystals and to inhibit segregation of the constituents.

Alloys and purpose. Printing alloys are formulated to meet the many and often widely different purposes of the industry; the principal considerations with a bearing upon these purposes are:

(a) Antimony associated with tin confers hardness.
(b) High antimony content, particularly in excess of the 12 per cent of the eutectic, extends the melting range.
(c) Tin is an expensive metal; it is therefore an economy to reduce the tin content where possible.

Measurement of hardness. For many printing purposes hardness is the most important consideration. There are several means of assessing this quality but the Brinell test is usually applied to printing alloys.

The Brinell test. A very hard steel ball, 10 mm in diameter, is

pressed into the surface of the metal under examination; the loading on the ball is 500 kg for soft metals such as the printing alloys. (The load is 3000 kg for hard metals.) The Brinell number is obtained from the formula

$$\frac{\text{Load}}{\text{Area of depression (sq. mm)}} \quad \text{(Table 15.1).}$$

TABLE 15.1. EXAMPLES OF ALLOY FORMULATIONS

Purpose	Sn (%)	Sb (%)	Pb (%)	Melting range deg C	(deg F)	Brinell no.
Electro backing	2	3	95	43	(109)	11·0
Slug casting	4	10	86	12	(22)	20·5
Stereo metal	7	15	78	22	(40)	24·0
Monotype	8	17	75	23	(42)	25·0
Type founding	18	28	54	92	(166)	38·0

(a) The formulations are representative only; they may be varied considerably around the proportions given.

(b) The arrangement is in order of increasing antimony content.

(c) It should be observed that hardness increases with antimony content.

(d) The melting range is not a temperature but the range over which melting (or freezing) occurs.

(e) Other than in the case of electro backing the melting range is extended as the antimony content is increased; the probable explanation of the anomaly is that with electro backing metal the small Sn–Sb content depresses the mean melting point very little compared with the other metals in the table.

(f) The type founder's metal may contain about 0·6 per cent of copper to increase the hardness.

Voids. These are air-filled hollows or bubbles in the cast which may result from imperfections during the casting operation. However, some voiding is inherent and it only becomes dangerous when excessive and when the hollows are near the printing surface; in the latter condition mechanical collapse is possible.

To examine the extent of voiding, the principle of Archimedes is applied (see Chapter 3). The density of the suspected cast and

that of the sound metal is obtained. The proportion of voids, expressed as a percentage, is calculated from the formula

$$\left(1 - \frac{\text{Density of suspected cast}}{\text{Density of sound metal}}\right) \times 100.$$

Depreciation of alloys in use. Tin is a slightly more reactive element than lead. While the position of antimony is rather anomalous, it behaves in this respect in much the same manner as lead.

Printing alloys are continually cast and re-cast, and thus the components are subject to oxidation. Tin is more freely oxidized than its companions while antimony—probably on account of its close association with tin—is normally somewhat in front of lead in this tendency. Therefore the dross removed from the molten alloys includes tin in excess of the other metals followed by antimony and lead. This wastage is corrected by replenishing the alloy with the components adjusted to the deficiencies.

Effects of impurities. Unwelcome accretions in the printing alloys are mainly derived from the scraps of zinc, copper, brass, and other metals always present in the printing house:

Zinc is a much more reactive metal than the alloy components. It very freely oxidizes to form a tough skin which hinders the flow into the mould; this is the most serious of the impurities and it has indeed been stated even one or two parts of zinc in 100,000 can be harmful.

Copper is the most usual contaminant of printing metals. As has been observed above, small quantities of this metal are considered advantageous in founder's metals, but for most other purposes the formation of a copper–antimony compound which separates as small crystals above the normal first solidification temperature can be disastrous. The orifices of the casting apparatus are partially choked and, since the action is cumulative, working may cease.

Other metals. Aluminium as an impurity is very similar to zinc; nickel, often from nickel-faced stereos, behaves in much the same manner as copper, but the effects are even more serious; iron is relatively innocuous.

Examination under the microscope. The crystal structure of an alloy is very obvious under the microscope. The flat face of a small specimen is prepared by treatment with progressively finer abrasive and finally given a mirror finish with a metal polish. To distinguish the components, the bright surface is bathed in a very dilute solution of silver nitrate with the effect that the whitish crystals of tin and antimony appear clearly against the darkened background of the eutectic. It is probable that the silver nitrate, an acid salt, very slightly etches the predominant lead of the eutectic and metallic silver in a fine state of division (as in a developed photographic plate) is exchanged for the lead removed—the latter metal is more reactive than the relatively inert silver. The process may be set down tentatively as

Pb	$+$	$2AgNO_3$	$=$	$Pb(NO_3)_2$	$+$	$2Ag$
Lead		Silver nitrate		Plumbous nitrate		Silver

Density of casting alloys. It might be supposed that the density (or specific gravity) of one of these alloys would be the average of the components calculated to the proportions present. In fact the structure of the alloy—the form and distribution of the crystals, the proportion of solid solution—all tend to counter any calculated value. Thus to cite a simple case the density of an aqueous solution of a salt such as cupric sulphate is lower than that of the arithmetic mean of the components. Given the densities of tin, antimony, and lead as 7·2, 6·6, and 11·3, respectively, the density of an alloy at 20°C may be 9·8 while the calculated density is 10·2.

(b) METALS OF PHOTOGRAPHIC REPRODUCTION

Introduction. The printing uses of these metals is considered elsewhere. Here it is proposed to deal briefly with their origins and properties in the context of their more obvious applications to the industry.

It is convenient to set down some of the most important of these properties in tabular form since these metals are used separately unlike those of group (a) (Table 15.2).

TABLE 15.2

	Cu	Zn	Mg	Al	Fe	Cr	Ni
Density (SG)	8·95	7·1	1·74	2·7	7·9	7·1	8·9
Melting point (°C)	1083	419	651	657	1535	1615	1455
Hardness (Brinell no.)	37	10	35	16	—	100	60

(a) Some other metals have been included for comparison; it should, however, be noted that chromium and nickel are electro-deposited on softer metals to give great surface hardness.

(b) The Brinell no. should be regarded as an approximation only—the hardness is subject to considerable variation during manufacture and processing. The hardness of iron is even more variable and no number is given.

(c) All the information refers to the pure metals; copper is used close to purity but zinc, magnesium, and aluminium may be regarded as alloys although the additions are a very small proportion of the whole and are likely to influence the physical constants by little but negligible amounts.

Copper. It may be said that man's familiarity with metals is related directly to their occurrence "native" or to the ease of extraction from the ores. Copper is in both these categories and it has thus been known from or before the "dawn of history". Copper is found as the metal in small quantities in many parts of the world, but the largest deposits in this form are at the western end of the North American Great Lakes. However, the chief source is chalcopyrite or copper pyrites (a copper-iron sulphide). Other ores include cuprite (cuprous oxide), copper glance (cuprous sulphide), and malachite (basic cupric carbonate)—the source of a beautiful green pigment.

Extraction. The reactions involved in smelting the chalcopyrite ores are rather complex; the ore is roasted in air:

(a) $2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2$

Chalcopyrite — Oxygen — Cuprous sulphide — Ferrous oxide — Sulphur dioxide

The ferrous oxide is removed by smelting with sand (mainly silica or silicon dioxide):

(b) $$\underset{\text{Ferrous oxide}}{FeO} + \underset{\text{Silica}}{SiO_2} = \underset{\text{Ferrous silicate}}{FeSiO_3}$$

The operations (a) and (b) may proceed simultaneously. The silicate is lighter than the fused cuprous sulphide and forms a slag on the surface; the molten sulphide with some metallic copper—the matte—is run off and subjected to further oxidation:

$$\underset{\text{Cuprous sulphide}}{Cu_2S} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Copper}}{2Cu} + \underset{\text{Sulphur dioxide}}{SO_2}$$

The sulphur dioxide produced in the process has many industrial uses including that of being a raw material of sulphuric acid.

Properties. Copper is a very beautiful metal of high ductility and malleability; it is an excellent conductor of electricity and heat.

The copper plates used in the photoengraving process are prepared by heavy rolling; in the final operations the plate is given an almost mirror polish on what will be the image face. The metal for this purpose is close to complete purity and, indeed, there has been a vogue for electrodeposited copper which may persist here and there.

The chief advantages of copper for photoengraving are:

(a) Its very fine grain or crystal structure, the size of the elements being about 0·025 mm $\left(\frac{1}{1000}\text{ in.}\right)$ in diameter.

(b) The dimensional stability of copper—much beyond that of zinc and magnesium—makes it particularly suitable for critical multicolour work.

(c) Reference to Table 15.2 will show that it is much harder than zinc although magnesium is not far behind.

The use of copper for photogravure is almost inevitable since it is the only metal really capable of satisfactory ferric chloride etching which is essential for the conventional process at least.

Copper is also one of the metals favoured in bi- and tri-metal photolithography.

Zinc. It is said that the Romans, although not aware of zinc as a metal, used copper and zinc ores together to prepare brass. The first undoubted recognition of zinc as a separate metal occurred early in the eighteenth century; several are credited with the discovery. The principal sources are zinc blende (sulphide) and calamine (carbonate) which occur widely in the United States, Australia, and in parts of central Europe.

Extraction. Both the ores cited above are first roasted in air to convert them to the oxide:

(a) $2ZnS + 3O_2 = 2ZnO + 2SO_2$

Zinc sulphide — Oxygen — Zinc oxide — Sulphur dioxide

(b) $ZnCO_3 = ZnO + CO_2$

Zinc carbonate — Zinc oxide — Carbon dioxide

The zinc oxide is heated with ground coke or coal; the metal comes off as a vapour which condenses on sheet iron placed over the retorts—this process (sublimation) is effective with only a few metals, among them cadmium and mercury of the same group of the periodic table.

Properties. Zinc is a brittle grey metal which is rather freely subject to oxidation; its crystals have an average diameter of about 0·125 mm $\left(\frac{5}{1000}\text{ in.}\right)$, giving a much coarser grain than copper. For photoengraving and photolithography pure zinc is somewhat too soft and it is chemically relatively inert or passive; therefore, for these purposes, it consists of 98–99 per cent with small quantities of cadmium, lead, iron, and magnesium. The Dow (powderless) etching process demands a much finer structure with, probably, some differences in composition. Metal of this type is marketed under various proprietary names, but there is a tendency to group them as microzinc.

Magnesium. The salts of this metal were known long before the isolation of the element; some of them are credited with medicinal

properties—Epsom salts (sulphate) and Magnesia alba (carbonate) are well known. Davy is said to have prepared an impure magnesium by electrolysis in 1808, but Bussy (1794–1882) isolated and identified the metal in 1829. Magnesium is highly reactive and thus it cannot be expected to occur in nature as the metal; its compounds, however, are very widely distributed, principally as magnesite (carbonate) and dolomite (calcium–magnesium carbonate); the latter forms many mountain masses—it is named from ranges in the eastern Alps. During the Second World War the need for the metal increased enormously and this led to the recovery of magnesium salts from the ocean.

Extraction. Magnesium is obtained by the electrolysis of the fused oxide or chloride; the former is prepared by the partial decomposition by heat of the carbonate:

(a) $MgCO_3 = MgO + CO_2$

Magnesium carbonate — Magnesium oxide — Carbon dioxide

The chloride may be manufactured by the action of hydrochloric acid on the carbonate or by the action of chlorine gas on the oxide in the presence of carbon and with considerable heat:

(b) $2HCl + MgCO_3 = MgCl_2 + H_2CO_3$

Hydrochloric acid — Magnesium carbonate — Magnesium chloride — Carbonic acid

(c) $MgO + Cl_2 + C = MgCl_2 + CO$

Magnesium oxide — Chlorine — Carbon — Magnesium chloride — Carbon monoxide

Electrolysis of either compound takes place in an iron cell which forms the cathode with carbon anode.

(d) $MgCl_2 \xrightarrow{\text{electrolysis}} Mg + Cl_2$

Magnesium chloride — Magnesium — Chlorine

Properties. Magnesium is a silvery white metal and it is the most reactive of those considered here. It burns with a brilliant blueish

white flame which gives abundant oxide—one of the standard whites. Although no reason has been advanced, magnesium is not used in photolithography, as far as is known, but it has considerable use in photoengraving; it was the original metal for Dow etching (see p. 290) but it has been partially replaced for this purpose by zinc.

Its structure should recommend it as a printing material—the grain is almost, if not quite, as fine as that of copper, and it is almost as hard. However, the fire hazard is deemed by some to be a substantial disadvantage although, in fact, unless it is finely divided or in thin ribbon form (as for photographic flash apparatus), it ignites with difficulty and is not much more flammable than zinc.

Magnesium in this context is considerably more alloyed with other metals than is zinc; what may be accepted as a standard or typical composition is:

Magnesium	Aluminium	Zinc	Manganese
95%	4·0%	1·0%	trace

Smaller amounts of iron, nickel and, more rarely, cadmium may be present.

Aluminium. Alum, a complex aluminium sulphate with other sulphates, was known in the classical world (hence the name of the metal) and its oxide or some of its salts are important in many precious stones. Aluminium is the most abundant of all metals in the crust of the earth, i.e. in that part which surrounds the core (the latter is believed to be metallic iron–nickel)—it is a component of all rocks both igneous and sedimentary; clays are complex aluminium silicates. It should be no surprise, therefore, although it almost always is, that this metal is so often combined with the two elements which precede it in order of abundance—oxygen and silicon.

For all that, aluminium is among the most recently known of the metals; its existence was suspected by many chemists, including the great Lavoisier, towards the end of the eighteenth century, but it was not isolated until 1827.

The only undoubted source of the metal is bauxite, an impure

aluminium oxide, although claims for its extraction from clay are made from time to time in Russia.

Extraction. The bauxite is subjected to an elaborate process of purification the product being alumina. The alumina is dissolved in molten cryolite (sodium aluminium fluoride)—the purpose of this action is to lower the very high temperature of fusion of the alumina alone. The molten compounds are electrolysed in an iron cell lined with graphite which forms the cathode, while carbon rods immersed in the liquid are the anodes. Since the electricity consumed is at an e.m.f. of 5·5 V at a current of about 100,000 A, this process is economical only in countries with abundant hydroelectric power such as Norway and France.

The actual course of the electrolysis is not fully known but it may be simply, and perhaps too simply, shown as

$$\underset{\text{Alumina}}{2Al_2O_3} \xrightarrow{\text{electrolysis}} \underset{\text{Aluminium}}{4Al} + \underset{\text{Oxygen}}{3O_2}$$

Molten aluminium collects at the base of the cell from which it is run off; oxygen appears at the anodes with which it slowly combines to form carbon monoxide and dioxide and, consequently, the anodes need replacement from time to time.

This process has alone made the abundance of aluminium available to the world; indeed, before the development of large-scale electricity and almost within living memory, aluminium was regarded as a rare curiosity.

Properties. Aluminium is a light white metal almost as active chemically as magnesium; it oxidizes readily but the coherent layer of oxide which forms inhibits further corrosion. While photoengraving uses have frequently been suggested with little or no effect, aluminium is probably the most favoured single metal for offset lithography. The pure metal is rather too soft for the purpose and it is consequently alloyed, as are zinc and magnesium, with other metals. However, as in the case of zinc and, with reservations, in the case of magnesium, the components other than aluminium are small in amount; indeed, aluminium plates are available consisting of 99 per cent of the metal. The addition of

small quantities of copper is likely to increase the mechanical strength of the plate, and this property is more important to prevent rupture at the plate retaining devices on the machine than the mere hardness of the image surface itself.

The properties of those metals used for offset lithography are considered in the matter on the chemical aspects of the process.

Electrodeposited metals. Various purposes of the industry are served by electrodeposited (or plated) copper, chromium, and nickel; the subject is considered in Chapter 18.

CHAPTER 16

Photographic Images on Metals

Introduction. It is hardly a matter for surprise that for the greater part by far of the history of printing in Europe (unfairly to omit China) manual methods alone were used to prepare illustrations, but it may be surprising that all these methods survive.

The woodcut, wood and soft-metal engraving are still employed in letterpress if mainly for limited editions. In intaglio printing, copper and steel plate engraving all but dominate the security field and have wide uses for the highest quality letter headings and visiting cards, while wet- and dry-point etching, mezzotint, and aquatint remain within the scope of the creative artist; in planographic printing the remarkable techniques of pure lithography are still practised for posters although often combined with photography (while examples of Victorian chromolithography have become collectors pieces). What is generally regarded as the parvenu among the processes—screen process or silk screen—is almost wholly manual and small scale in spite of some remarkable examples of applied photography while, as serigraphy, it is favoured by many original artists.

Photographic processes of reproduction. Photographic methods have been widely used for considerably less than a century although, as considered in Chapter 14, the first photoengraving —it should be photoetching—actually preceded the first permanent photograph. This was the heliogravure of Nicéphore Niepce and the year was 1824. The light-sensitive properties of a certain variety of bitumen were used to obtain a print on metal from an

engraving; the image was the reverse of the original and consequently it was etched to provide an intaglio plate. Thus bitumen was the earliest of the materials employed to prepare a photographic image on metal as a stage in the making of a printing surface—perhaps, indeed, the most distinctive stage since the more photographic operations which precede it are often little different from pure photography.

Bitumen. Niepce's bitumen process remained in use or perhaps was rediscovered since it was certainly practised towards the end of the nineteenth century. All instruction manuals of the period describe it and the process very likely survives somewhere since it appears capable of producing line images of very high quality.

As far as is known, the light-sensitive properties have never been investigated; bitumen consists of an indeterminate mixture of hydrocarbons, but for the purpose under discussion Syrian or Judean bitumen (or asphaltum) is almost unique. It may be very tentatively suggested that this variety contains some complex unsaturated hydrocarbons which polymerize with the prolonged exposures to light needed for the purpose perhaps in the presence of activating minerals.

Dichromate–Colloids. Mungo Ponton is credited with the discovery in 1839 of the insolubilizing action of light on a dichromate–colloid mixture although it seems likely that he was anticipated by at least one of his contemporaries who, however, failed to recognize its importance.

It may be said with some certainty that the discovery alone made the photographic processes possible since the earlier bitumen process was far too slow and perhaps rather unreliable. Be that as it may, there is no doubt that the dichromates must be ranked as among the most valuable of materials in the field.

Colloids. A definition is given in Chapter 11. Here it is proposed to consider the printing importance and some of the applications of these substances in graphic reproduction:

(a) *Albumen.* Dichromate–albumen is used with an ink top to provide the image on metal in photoengraving, particularly for line etching by the manual rolling-up method for which it has

considerable advantages; it cannot, however, be used for powderless etching since the bath additives would destroy the ink–bitumen resist. Albumen is also used to prepare surface plates for photolithography. The albumen is obtained from white of egg or as the dried substance which is made from the same source. Albumen is largely protein, a very important group of compounds essential as foodstuffs and as the basic materials of life itself. The molecule of a protein may be built of many thousands of amino-acid units, and the products must be classed as among the most complex of organic substances. The simplest acid of this type is amino-acetic acid or glycine; it is formed by the replacement of one of the non-acid hydrogen atoms of the parent compound by the amino group (—NH_2):

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{-H+NH_2} \underset{\text{Amino-acetic acid}}{CH_2NH_2COOH}$$

(b) *Fish-glue.* This is almost certainly the most widely used colloid for halftone photoengraving; the necessary burning-in or stoving, however, while deemed an advantage on copper, is rather a drawback for zinc since the temperature reached for the purpose (320–350°C) is close to the point where the metal becomes structurally weak and, unless carefully controlled, may actually rise to the melting point. Fish-glue for this purpose is manufactured from the waste materials of the fish processing industry. It is also largely protein and chemically is not greatly different to albumen.

(c) *Gum-arabic.* In the deep-etch process for the preparation of plates for offset lithography it is necessary to use a light-sensitive coating on the metal to form an easily removable stencil; dichromate–gum-arabic serves this purpose admirably. This material is an exudation of certain varieties of acacia (hence it is also 'gum-acacia') which fluorish in semi-arid regions of the Sudan, Upper Egypt, and Arabia. The composition of gum-arabic remains uncertain, and it is likely that it is a mixture of a number of substances of closely similar structure; it is usually said to be a mixture of arabic acid, and the calcium, magnesium, and potassium salts of that acid together with calcium and potassium carbonates. Various empirical formulae have been suggested for

arabic acid among the simplest of which is $C_{23}H_{38}O_{22}$. However, on treatment of the gum with a mineral acid, arabinose (chemically a sugar but not necessarily sweet) is isolated; this substance has the rather more manageable abridged structural formula $CH_2OH(CHOH)_3CHO$.

(d) *Shellac.* This material in its natural state is a resin rather than a colloid as defined, but, boiled with alkali carbonate or treated with ammonia it becomes water miscible in the manner of a true colloid; in this condition with dichromate it is used for "cold-top" enamel—a resist with advantages in photoengraving since, as implied by the name, it needs a relatively low heat of stoving. Shellac is a natural resin produced or secreted by the lac insect which lives on certain trees fairly common in South-east Asia. Shellac, again, is very complex chemically. It consists of a number of polyhydroxy acids which may be represented by the empirical formula $C_{16}H_{32}O_5$ together with small quantities of wax. The simplest hydroxy acid is $CH_2(OH)COOH$ hydroxyacetic acid (glycollic acid), in which one of the non-acid hydrogen atoms is replaced by the hydroxyl group.

(e) *Gelatin.* The image-carrying material in the photogravure process is dichromate–gelatin; here there is a clear distinction to the companion processes in which the image structure is either wholly present or absent. In standard gravure gradation is represented by variable thickness (or variable permeability) of gelatine with the uniform screen imposed over all. There are, however, variants of the normal process which approach more nearly photoengraving and photolithography in image formation. Collotype is often held to be the most beautiful of all illustrative processes; it also uses dichromate–gelatin, but this is treated to give a fine granular structure by reticulation of the gelatin. It is a planographic process in which the printing surface accepts water inversely as exposure and thus receives ink at a maximum at the fully exposed zones and at a minimum in the areas of least exposure (the highlights). The standard photostencil in screen process is produced in dichromate–gelatin, but here the image bearing areas are completely removed in warm or hot water. Phototransfer papers are basically dichromate–gelatin on a support; the image

is hardened by exposure through a negative; the non-exposed gelatin is moisture receptive and thus the image will selectively accept transfer ink which is laid down on stone or plate. While this method remains as an auxiliary it has naturally declined in favour of photolithography direct to metal. Gelatin is a very complex protein prepared from animal bones and tissues; unlike albumen and fish-glue its solution in water sets as a jelly in the cold.

(f) *Polyvinylalcohol.* All the preceding vehicles for the dichromates are of natural origin; PVA is synthetic. It is used in photoengraving as an alternative to fish-glue and, to some extent, to albumen; it is also in some use for surface offset lithography. There is, however, no doubt that its greatest value is for the preparation of line and halftone plates for powderless etching—it has a relatively low temperature (about 250°C) of stoving and thus the often large zinc and magnesium plates may be kept flat and, unlike fish-glue, it is almost scum-free.

Although PVA is readily dispersed in water and conforms to definition as a colloid, its formula supports the view that it is a resin. It has been briefly considered in Chapter 13. PVA is a polymer of the formula $(H_2C = CHOH)_n$ which is subject to further stages of polymerization during the preparation of images on metal. The majority of PVA resists in use are proprietary although formulae are available for compounding them from the raw materials.

The dichromate–colloid reaction. There are many dichromates available for the present purpose since the importance of these compounds rests upon the acidic group; the basic radicle is of lesser consequence unless it is likely to react with other components of the light-sensitive coatings. However, in practice the ammonium salt $(NH_4)_2Cr_2O_7$ is preferred for photoengraving and photolithography, while the potassium compound $K_2Cr_2O_7$ is in general use for photogravure.

The mechanism of the hardening or insolubilizing action of light upon dichromate–colloids is rather uncertain. The dichromates are vigorous oxidizing agents and thus, in this function, they are themselves reduced, the products being various oxides or hydroxides of chromium or, in acid solution, salts of chromium.

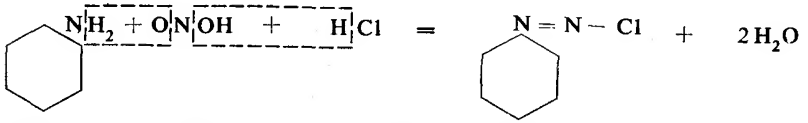
The dichromates are stable in the dry crystalline state but, in

the presence of colloids, they undergo considerable decomposition when exposed to light (the effective radiation is strictly ultraviolet and, to a lesser extent, the shorter wavelengths of visible light). It is also of importance that the action occurs or continues in the absence of light; this is the dark effect or dark reaction the practical consequence of which is to rule out the storage of coated plates for other than brief periods. However, the dark effect is largely inhibited or retarded in the cold, and limited storage is possible in a refrigerator. It is clear, nevertheless, that the colloids themselves take part in the action. It is suggested that the dichromate is reduced to chromic oxide (also known as sesquioxide) Cr_2O_3, and that this substance promotes or activates the hardening of the colloid by further stages of polymerization. Evidence for the presence of this oxide is advanced by some observers who have noted a greenish colour in the hardened image; chromic oxide is indeed green.

The images formed by fish-glue (enameline) and PVA are further hardened by stoving. There is little doubt that in this final state the images are thermosetting, i.e. irreversible, plastics.

Presensitized plates. All the image-forming materials briefly examined above are dichromate-sensitized colloids. A completely novel range of materials has been developed since the Second World War although many were proposed earlier. These substances are only novel in their applications to the graphic arts since the most important are based on the diazo reaction discovered by Peter Gries in 1858.

The simplest diazo compound is the result of the reaction in the cold between aniline and nitrous acid in the presence of hydrochloric acid:



Aniline (aminobenzene)	Nitrous acid	Hydrochloric acid	Benzene diazonium chloride	Water

(Other structures have been proposed for the diazo compound.)

The diazo compounds are, in general, very unstable and/or highly reactive. The example given and many closely related compounds readily couple with a number of other organic substances to form the important group of azo dyes (azo, diazo, etc., from an earlier word for nitrogen still current as *azote* in France).

For the purposes of graphic reproduction, diazo compounds have been prepared with many and sometimes opposed properties:

(a) Decomposed by light: the decomposition product insolubilizes its colloid vehicle therefore giving a positive image from a negative.
(b) Decomposed by light: the decomposition product inert while the original compound, suitably treated, insolubilizes its colloid vehicle therefore giving a positive image from a positive and negative from a negative.
(c) The light decomposed product itself forms a stable insoluble image therefore giving a positive from a negative.
(d) The original compound is insoluble and capable of forming a stable image. The exposed compound is decomposed and readily removable; therefore a positive is given by a positive and a negative by a negative.

In spite of the instability, diazo-sensitized plates may be safely stored in suitable conditions almost indefinitely.

While diazo compounds are dominant, other materials are available—notably complex derivatives of cinnamic acid.

Other image materials. The non-image areas of dichromate–gelatin are capable of accepting water while the fully exposed and hardened image is almost impermeable. The early swelled-gelatin processes used this property to prepare relief images directly, the contoured gelatin being employed as a matrix for stereo- or electrotyping. Closely related were the wash-out gelatin processes in which the non-image areas were removed in hot water leaving the image in relief.

Both of these methods have been revived from time to time; a successful modern process of the second type is known as colloplate, in which the colloid is supported on a flexible metal base for use on small, rotary letterpress machines.

Several photopolymers have been introduced for the direct production of relief plates. The best known is Dycril in which the monomer or low polymer, supported on its steel or aluminium base, is exposed in contact with a negative to a powerful light source. The material receiving the light is high polymerized through to the base; the unexposed non-image zones are removed by dilute sodium hydroxide directed to the plate as a spray under pressure. The result is an almost indestructible image in adequate relief with ink-receptive qualities, it is claimed, superior to any metal.

Dycril material is strictly proprietary and its nature is not fully disclosed, but it may be considered as being of one or other of the types discussed above.

Optimum conditions of working. Changes in temperature, humidity, concentration, and pH values effect changes in the dichromate colloids. Since presensitized plates are used directly from sealed packages, they are little influenced by these changes, and this is regarded as among their merits.

Temperature. The majority of chemical reactions proceed more rapidly as the temperature rises; the hardening of dichromate–colloids is mainly if not wholly a chemical reaction.

Humidity. Water also accelerates most reactions particularly when the components are in solution. While the dichromate–colloids are not in solution when coated on their support, water is present and if further water is made available by rises in atmospheric humidity the reaction is accelerated. Thus rises in temperature and humidity confer rises in sensitivity and consequently air conditioning is desirable (if not completely necessary) to maintain uniformity.

Concentration. The velocity of a reaction is directly related to the availability of the reactants. Thus increase in the quantity of dichromate, within limits, increases sensitivity, but, since the dark reaction is also accelerated, shelf-life is shortened.

pH. The sensitivity of coating solutions increases from about pH 8 to pH 4 but the extreme acid condition is not desirable since stability is lessened and tendency to scum increased. Ammonium dichromate is a salt of an almost strong acid and a weak base,

and it has a pH value of about 4·4 at the concentrations in use. Potassium dichromate is near to neutrality, rather surprisingly perhaps, at the usual concentration. Solutions of albumen, fish-glue, and PVA as normally employed are all close to neutrality; gum-arabic is markedly acid at about pH 4·2, while shellac as treated is rather alkaline at pH 8. Gelatin is not used as a solution as defined but it also is close to the neutral point.

The optimum pH value of all the dichromate–colloids is from 6·2 to 6·5; therefore most of these coating materials need some adjustment when the ammonium salt is used. This adjustment may be effected by the cautious addition of ammonium hydroxide and this is normally practised.

However, while some ammonia is retained by the coating a little is lost during the drying, and consequently the pH value tends towards rather greater acidity. The dichromate–gum solution apparently needs more adjustment in this context than any of its companion materials. It is necessary to recall that the gum image serves a somewhat different purpose in deep-etch photolithography.

CHAPTER 17

Chemistry of Etching

Introduction. Etching is defined for the present purpose as the removal of parts of the surface of a metal by the action of an acid or acid salt; the result is an image in relief for letterpress printing or an image below the metal surface for intaglio printing. The image in deep-etch photolithography is also eroded but this is not regarded as characteristic of the process since the depressions are usually filled in with a hard impervious material which forms the actual printing area.

The so-called etching of the non-image regions of a litho plate to render it water-receptive does not conform to the definition above; it is considered in Chapter 19.

The metals principally employed are zinc, magnesium, and copper for photoengraving; zinc and aluminium for photolithography; and copper for photogravure.

THE MORDANTS

Nitric acid. The acid as supplied for commercial use is about 60 per cent HNO_3; it is possible to remove the 40 per cent water by chemical means but, since the acid is rarely used in high concentrations, this is an unnecessary expense.

The older process for the manufacture of nitric acid is by the action of sulphuric acid on sodium nitrate; while the process is in decline it is widely used for laboratory preparation:

$2NaNO_3$	+	H_2SO_4	=	$2HNO_3$	+	Na_2SO_4
Sodium nitrate		Sulphuric acid		Nitric acid		Sodium sulphate

The sodium nitrate for the commercial process is quarried, as caliche or schile altpetre, in the Atacama Desert of northern Chile; its chief use is, however, as a fertilizer.

The dominant modern process for the production of the acid is the oxidation of ammonia, the latter being synthesized from its elements. The whole must be ranked among the most elegant techniques of chemical engineering:

(a) *Preparation of ammonia*

$$N_2 + 3H_2 \xrightarrow[\text{high temperature}]{\text{high pressure}} 2NH_3$$

Nitrogen Hydrogen Ammonia

The action is catalytic. A catalyst is defined as a substance which promotes or accelerates a chemical reaction and which is itself unchanged at the end of the process. Catalysts are usually metals in a fine state of division or metallic oxides.

The ammonia resulting from the action is a gas; the liquid commonly known as ammonia is ammonium hydroxide, which may be regarded as a solution of the gas in water although it is strictly a compound, NH_4OH, with water.

(b) *Oxidation of ammonia*

$$4NH_3 + 5O_2 \xrightarrow[\text{catalyst}]{\text{very high temperature}} 4NO + 6H_2O$$

Ammonia Oxygen (from air) Nitric oxide Water

(c) *Oxidation of nitric oxide*

$$2NO + O_2 = 2NO_2$$

Nitric oxide Oxygen (from air) Nitrogen dioxide

This stage occurs during the cooling from the high temperature of the preceding reaction.

(d) *Nitric acid*

$$\underset{\text{Nitrogen dioxide}}{4NO_2} + \underset{\text{Water}}{2H_2O} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Nitric acid}}{4HNO_3}$$

This equation represents the reaction in the simplest terms; as is usually the case the whole process is much more complex than is suggested by this summary.

Ferric chloride. This salt is made by the direct combination of its elements:

$$\underset{\text{Iron}}{2Fe} + \underset{\text{Chlorine}}{3Cl_2} \xrightarrow{\text{heat}} \underset{\text{Ferric chloride}}{2FeCl_3}$$

The reaction is, in effect, burning, and, although heat is necessary to initiate the process, it continues spontaneously to completion.

ETCHING OF THE METALS

Zinc. This metal is used in the United Kingdom for line and coarse screen halftone—it is seldom considered suitable for fine screen although excellent work, including colour, is produced in many European countries on zinc; it is also one of the principal metals for offset lithography.

In terms of the chemistry of the process any of the strong mineral acids may be used for etching, but in practice nitric acid is preferred; although no chemical or physical explanations have been advanced (as far as is known), it is said to etch more smoothly.

The simplest statement of the action of nitric acid on zinc is

$$\underset{\text{Nitric acid}}{2HNO_3} + \underset{\text{Zinc}}{Zn} = \underset{\text{Zinc nitrate}}{Zn(NO_3)_2} + \underset{\text{Hydrogen}}{H_2}$$

which suggests the standard and typical action of acid and metal; this is, again, too simple to indicate the involved happenings which result.

Nitric acid differs from its companion mineral acids in being an active oxidizing agent, which means that it is freely subject to

reduction; the hydrogen evolved is, momentarily as nascent, very reactive; some of the probable consequences are indicated:

(a) $2HNO_3 + H_2 = 2NO_2 + 2H_2O$
Nitric acid — Hydrogen — Nitrogen dioxide — Water

(b) $2HNO_3 + 3H_2 = 2NO + 4H_2O$
Nitric acid — Hydrogen — Nitric oxide — Water

(c) $HNO_3 + 4H_2 = NH_3 + 3H_2O$
Nitric acid — Hydrogen — Ammonia — Water

Other probable products are (d) ammonium nitrate (NH_4NO_3) (e) hydroxylamine (NH_2OH) and nitrogen tetroxide (N_2O_4). The latter is the chief constituent of the pungent brown gas which is very evident when zinc is treated with highly concentrated nitric acid.

Magnesium. Magnesium as an alloy is well known as the first successful metal for powderless etching (see below). It is divalent in simple reactions and, for the present purpose, since nitric acid is the usual mordant, the reactions taking place during etching are those given above for zinc; it is, of course, necessary to substitute the symbol for magnesium for that of zinc.

Copper. Ferric chloride is the universal mordant for copper in the photoengraving and photogravure processes. It is possible to set down the reaction between the salt and the metal in a deceptively simple form:

$FeCl_3 + Cu = FeCl_2 + CuCl$
Ferric chloride — Copper — Ferrous chloride — Cuprous chloride

The ferric chloride hydrolyses to the acid and it therefore might be supposed that the reaction is that normal between a metal and a strong acid. However, hydrochloric acid acts far too slowly to be of use for the purpose. H. L. Howard showed in 1959 that, at the concentrations employed for etching, the dissociation of the salt is greater than that of the acid at the equivalent concentration, and he advanced this to account for the abnormal behaviour of ferric chloride.

At the same time H. E. Rupp proposed an alternative hypothesis; iron is trivalent here and in its transition to the divalent state as shown in the equation above it exerts an oxidizing influence, being itself reduced:

$$\underset{\text{Ferric ion}}{Fe^{+++}} + \underset{\text{Copper}}{Cu} = \underset{\text{Ferrous ion}}{Fe^{++}} + \underset{\text{Cuprous ion}}{Cu^{+}}$$

This equation in ionic form and using the basic radicles only, expresses this hypothesis very clearly.

Deep-etch photolithography. The exposed photoresists of photoengraving are held very tenaciously on the metals even if not stoved (or burnt-in); the deep-etch litho negative image or stencil adheres weakly to the metal since it must ultimately be removed without trace. While the dichromate fish-glue or PVA unexposed areas are dissolved by the vigorous action of running water, the development of the deep-etch image is critical—it is usual to treat the plate with saturated or near-saturated solutions of calcium and/or zinc chloride ($Ca/ZnCl_2$) with a feeble organic acid such as lactic ($CH_3CHOHCOOH$) to lessen the risk of weakening the stencil.

The etching of the image through the stencil, often alcohol dried, is also a rather delicate operation; various chlorides are used—$CaCl_2$, $FeCl_3$—with hydrochloric acid, all calculated to form a solution near to saturation, again with the object of maintaining the stencil during the reactions.

These mordants are often proprietary and there are usually modifications for use on zinc or aluminium; using ferric chloride and hydrochloride acid for examples of the reactions:

$$\underset{\text{Ferric chloride}}{6FeCl_3} + \underset{\text{Aluminium}}{2Al} = \underset{\text{Ferrous chloride}}{6FeCl_2} + \underset{\text{Aluminium chloride}}{2AlCl_3}$$

$$\underset{\text{Hydrochloric acid}}{6HCl} + \underset{\text{Aluminium}}{2Al} = \underset{\text{Aluminium chloride}}{2AlCl_3} + \underset{\text{Hydrogen}}{3H_2\uparrow}$$

$$\underset{\text{Ferric chloride}}{2FeCl_3} + \underset{\text{Zinc}}{Zn} = \underset{\text{Zinc chloride}}{ZnCl_2} + \underset{\text{Ferrous chloride}}{2FeCl_2}$$

Copperizing. Cupric chloride, with a water-free alcohol as solvent, appears in some formulae chiefly—but not exclusively—for use on aluminium. While this is an acid salt, its principal function is the deposition of copper into the etched hollows since it is held that copper is more appropriate for the image than aluminium (see Chapter 19, under "Metals, oils, and water").

$3CuCl_2$	+	$2Al$	=	$2AlCl_3$	+	$3Cu$
Cupric chloride		Aluminium		Aluminium chloride		Copper

DOW (POWDERLESS) ETCHING

Introduction. In the manual methods of line etching it is necessary to protect the edges of the image as the acid erodes downwards since without some protection the image would be thinned or even destroyed. Consideration of the highly skilled craft is beyond the scope of this work.

During the Second World War magnesium was produced in enormous quantities and, with the end of that conflict, manufacturers were left with valuable plant and little use for the product.

The Dow Chemical Corporation of the United States established a research organization to promote new uses for magnesium. In 1949 consideration of printing metals was initiated and, later, the American Newspaper Proprietors Association became involved also in the investigation.

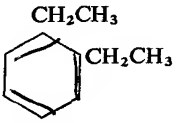
Before dealing with the subject in more detail a summary of the resulting Dow process may be an advantage.

Materials are added to the etching solution which, if undisturbed, form an acid-resistant film over the surface of the plate. The spray of acid directed to the plate breaks the film or inhibits its formation on the non-image areas; the filming materials are forced to the edges of the image as they become exposed by the action of the acid and in this manner the image is protected; the action is continued until adequate depth is attained.

The Dow process. The additives consist of two functional components; the patents cover a wide range of each but it is

proposed to consider the best known which are probably the basis of most of the available commercial products:

(a) *A light oil.* This is an aromatic hydrocarbon



Diethylbenzene

The ortho substituted compound is shown but, since the orientation of the substituents has not been given, it is likely that the differences, if any, in the three possible compounds is of little consequence.

(b) *A wetting agent.* Soaps and the so-called detergents function large as wetting agents. The substance used for the present purpose may be classed as the latter, and chemically it is strictly a detergent. Wetting agents are compounds which lower the surface tension of a liquid (surface tension is considered elsewhere). This substance is set down in general terms as an ester of sodium sulphosuccinic acid, the alcohol having from four to twelve carbon atoms; a specific example is di-isobutyl sodium sulphosuccinate:

$$\begin{array}{l} CH_2.COOC_4H_9 \\ | \\ CH.COOC_4H_9 \\ | \\ SO_3Na \end{array}$$

(this is the monosulpho-compound).

(a) and (b) together constitute the filming agent; the particles formed may be considered as typical of an emulsion and, also characteristic of some emulsions, they tend to aggregate. Gelatin appears in many of the Dow additives; there is some uncertainty about its purpose but it is generally held to act as a frothing agent which tends to prevent or retard the aggregation mentioned above.

While the object of the Dow research was to find uses for magnesium, and this indeed was the original metal of the process, it very quickly appeared that zinc was equally effective with some small modifications of the formulae—none of them fundamental.

The essentials of the etching machine. All the machines in use are specifically designed for the process; there are certain criteria which must be accepted:

(a) The acid, whether projected by paddles or nozzles, should make contact with the plate as near to the vertical as possible. (This provision was considered vital upon the inception of the process; today, while observed generally, it is not deemed to be of the original importance.)
(b) The optimum temperature of operation is from 18°C to 21°C (65–70°F); this is achieved by electric heating where necessary at the start of the action followed by cooling by refrigeration or cold-water circulation since the reaction of acid on the metals is highly exothermic.
(c) Fume extraction since many of the gases produced are a health hazard; this applies to all methods of etching which use nitric acid.
(d) Continuous agitation of the mordant when the apparatus is not in use to prevent the aggregation of the additive.
(e) Irregular rotation or oscillation of the plate to distribute the acid action uniformly over the whole.
(f) Means of controlling rate of paddle revolution or force of ejection by the nozzles since the power of impact of acid on the plate influences the velocity of etching.

Explanations of the Dow process. Two hypotheses are advanced to explain this remarkable and revolutionary etching process; they are not fully convincing or mutually exclusive:

(a) The first is the splash-force hypothesis suggested in its original form by the Dow organization; the more or less vertical impact of the acid on the plate forces the filming agent towards the margins of the image (any photoresist has a slight relief before etching starts). The build-up of the protective film is continuous throughout.

(b) The differential-heat hypothesis rests upon the fact of the great heat generated during the action. Although the cooling device may be completely efficient, this heat must persist briefly in and near the non-image zones with the result that the protective emulsion is displaced or partially disrupted while at the relatively much cooler image, and at the exposed shoulders the film is able to carry out its protective function.

Powderless etching of copper. Attempts have been made, with uncertain success, to apply the principle to the etching of copper. The mordant is the familiar ferric chloride and the usual additive thiourea ($CS(NH_2)_2$). It is stated that the additive, or the additive and the ferric chloride, forms a gelatinous film over the plate and that this film is selectively displaced in much the same manner as in the Dow process on magnesium and zinc; the chemistry of the action is, however, still obscure.

Electric etching. An inversion of electrodeposition is very successfully applied to the etching of copper, but attempts with other metals have failed as a whole. Etching in this context is perhaps a misnomer since the plate undergoing the action forms the anode (the positive electrode) of an electroplating system; this subject is more fully considered in Chapter 18.

CHAPTER 18

Electrodeposition

Introduction. Under the heading "Electrolysis" (p. 205) in Chapter 11 it is shown that the passage of an electric current through a fused electrolyte or solution of an electrolyte results in the partial, or even total, decomposition of that compound; it is further shown that this action is the implication of the word "electrolyte".

Electrodeposition or electroplating is a specific application of electrolysis; it is defined as the liberation of a metal from a solution of its salt usually for the purpose of depositing a layer of that metal on another metal or other surface made electrically conductive.

Many industries have found uses for electrodeposition and printing is among them; the applications to the latter are considered in some detail below.

The electrolytes in general. In principle, almost any salt of the metal to be deposited may be used but in practice, established by long experience and supported by some experimental evidence, the choice is limited, often to one or two compounds of each metal.

pH of depositing solutions. Many or most of the compounds in use give acid solutions by hydrolysis, and small amounts of mineral or organic acids appear in almost all the formulae. There is, however, considerable variation in pH values between the electrolytes —they range from just acid at pH 6 to markedly acid at pH 4·2 with an average in the neighbourhood of pH 5·5. A few electrolytes, some cuprous cyanide formulae among them, operate in the alkaline range pH 10 onwards.

Addition agents. Substances, mainly organic and largely colloidal, are often added to the electrolyte to promote, it is stated, smoothness and brightness in the deposit. These substances include glue, gelatin, albumen, various sugars, and thiourea. No wholly satisfactory chemical explanation for the action of these additives has been advanced, but it is suggested that small amounts are co-deposited with the metal and that consequently the normal crystal growth is restricted to give finer structures to the platings.

Wetting agents appear in many of the formulae with a more obvious purpose since they will tend to adjust differences in surface tension between the electrolytes and some of the cathode materials.

Agitation. Since the process of deposition involves the decomposition of the electrolyte at the electrodes, the electrolyte is momentarily depleted. It is consequently considered desirable to provide air-blast or mechanical agitation to the vat.

Reversal of polarity. In some electroplating processes advantages are claimed for brief periodic reversals of polarity, the balance being, of course, predominantly in favour of the desired direction of deposition. It is claimed that the practice restricts crystalline growth to give a finer and harder structure.

Bonding of deposit to the base. A successful bond or union between a metal being plated and the deposited metal is achieved when the pair tend to form a true alloy. Where this compatibility does not exist, an intermediate metal which conforms to the condition is thinly deposited first. Thus in the silver plating of iron or steel it is preceded by copper and in the nickel and chromium facing of printing surfaces a copper "flash" is laid down first (unless, of course, the surface, halftone, or gravure cylinder, is already of that metal.

Chemical equations. It is desirable to repeat with the matter below in mind that chemical equations normally represent the probable reactions in the simplest form: they do not necessarily state the complete sequence of events since variable side reactions may occur according to the conditions—principally the concentration of the reactants and the temperature.

THE DEPOSITED PRINTING METALS

Copper. The most important of all the deposited metals for printing is copper, and this is probably true for all industry. The deposition of this metal is much less difficult than others and its salts are abundant and cheap.

Copper is used for electrotype shells when it is laid down on a variety of moulds—natural and synthetic waxes and plastics which must be made electrically conductive by treatment with graphite (or blacklead) or by the chemical precipitation of silver or sometimes copper. Lead moulding is also practised, but its use is largely confined to halftone since the high pressure needed almost rules out the moulding of type. The metal is also deposited to form gravure cylinders, on stainless steel in one form of bimetal plate in photolithography, and on the metal base of the so-called trimetal plates of that process, the third metal being the chromium put down on the copper.

In aqueous solution, cupric sulphate as the salt of a strong acid is largely or wholly dissociated into sulphate ions carrying two units of negative charge and cupric ions with two positive charges:

$$CuSO_4 \xrightarrow[\text{water}]{\text{dissociation}} Cu^{++} + SO_4^{=}$$

The initial stages of the process of electrolysis of this solution is conveniently shown in Fig. 18.1:

(a) On the passing of the current the anode is positively charged and the cathode negatively charged.
(b) The positive cupric ions move to the electrode of opposite sign, the cathode, there to be discharged to assume the metallic state, and are deposited on that electrode.
(c) The negative sulphate ions travel to the positive anode of copper and, with the metal from the electrode, cupric sulphate is reconstituted.
(d) The process therefore may be considered to be in effect the transfer of copper from the anode to the cathode, and, if continued to the limit, the anode is destroyed.

In the practice of electrodeposition a small quantity of sulphuric acid is added to the solution; this provides a slight excess of sulphate ions and raises conductivity a little by the presence of hydrogen ions.

The above electrolyte is normally employed for the thicker

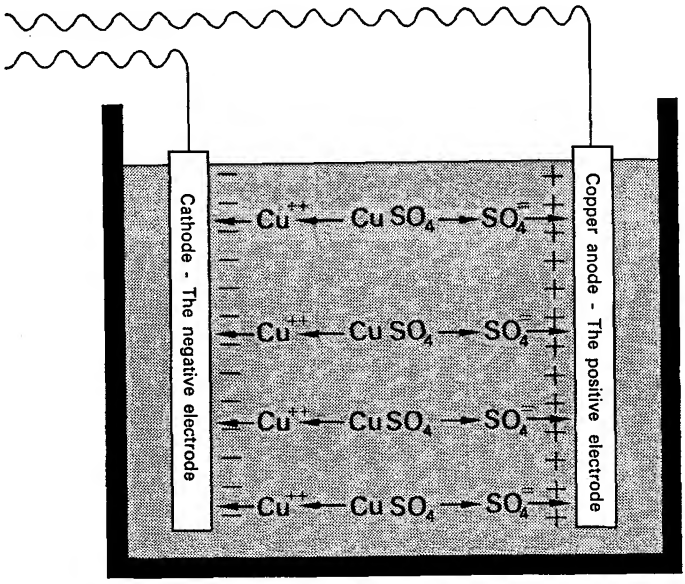


FIG. 18.1. The electrolysis of cupric sulphate.

copper deposits of electrotyping and gravure cylinders. The alkaline cuprous cyanide bath is used chiefly for the "flash" or "strike" deposit of the metal as a preliminary to the laying down of a further metal.

Cuprous cyanide (CuCN) has little aqueous solubility, but it forms a soluble complex with an alkali cyanide:

CuCN	+	NaCN	=	$NaCu(CN)_2$
Cuprous cyanide		Sodium cyanide		Sodium cuprocyanide

For optimum operation this electrolyte functions with a small excess of the cyanide radicle (via NaCN) and in the presence of a little sodium carbonate (Na_2CO_3) or other alkali.

The process of copper deposition may be represented as

$$NaCu(CN)_2 \xrightarrow{\text{electrolysis}} Cu^+ + \text{electron} = Cu$$

$$Cu^+ + CN^- = CuCN$$

$$Na^+ + CN^- = NaCN$$

Sodium cuprocyanide — Cathode — Copper anode

followed by reformation of the cuprocyanide as above.

Rochelle salt appears in many formulae; this is potassium sodium tartrate:

$$\begin{array}{l} CH(OH)COOK \\ | \\ CH(OH)COONa \end{array}$$

The function of this organic salt is to prevent the precipitation of cupric hydroxide ($Cu(OH)_2$) (the existence of the cuprous compound is doubtful) by the formation of a soluble copper complex derivative of tartaric acid. It should be observed that, in deposition from cyanide, the metal is monovalent.

Nickel. The principal use of this metal in printing is to provide hard and durable facing for metal and plastic stereos and for electrotype shells; it also adapted as an alternative to chromium for the facing of gravure cylinders.

The chief component of the electrolyte probably generally favoured is nickel sulphate ($NiSO_4$), but nickel ammonium sulphate ($Ni(NH_4)_2(SO_4)_2$) and nickel sulphamate ($(NH_2SO_2O)_2Ni$), the latter being the salt of an organic acid, are also widely in use. Nickel chloride ($NiCl_2$) and boric (or boracic) acid (H_3BO_3) appear in many of the formulae. The present discussion is confined to the sulphate, but the action of the other compounds may be shown if the double salt is considered as $NiSO_4.(NH_4)_2SO_4$ and if the sulphamate radicle is substituted in the equation below.

$$NiSO_4 \xrightarrow{\text{electrolysis}} Ni^{++} + SO_4^{=}$$

Cathode — Anode

The remainder of the process is exactly analogous to that of the electrolysis of cupric sulphate.

Chromium. The dominant purpose of chromium deposition in printing is the provision of the hardest and most durable surfaces for gravure printing and for letterpress printing from stereos, electrotypes, and photoengravings. It is also a constituent of multimetal lithographic plates. Chromium may be deposited directly upon copper plates, cylinders, and electros, but since the electrolyte reacts with stereotype metals these must be protected by deposited copper and/or nickel.

The chemistry of chromium deposition exhibits features not present with that of the metals discussed earlier. The principal material is not a salt but an oxide and, since it is wholly an acidic oxide, the metal initially forms part of the negative or acidic radicle in solution. This substance is chromium trioxide (CrO_3), often erroneously called chromic acid; since, however, it actually gives this acid in aqueous solution it is also correctly known as chromic anhydride.

$$\underset{\text{Chromium trioxide}}{CrO_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Chromic acid}}{H_2CrO_4}$$

It is probable that the next in the series of acids of chromium is the principal product:

$$\underset{\text{Chromium trioxide}}{2CrO_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Dichromic acid}}{H_2Cr_2O_7}$$

The immediate action on electrolysis is

$$\underset{\text{Chromic acid}}{H_2CrO_4} \longrightarrow \underset{\text{Cathode}}{2H^+} \quad \underset{\text{Anode}}{CrO_4^{=}}$$

$$\underset{\text{Dichromic acid}}{H_2Cr_2O_7} \longrightarrow \underset{\text{Cathode}}{2H^+} \quad \underset{\text{Anode}}{Cr_2O_7^{=}}$$

Dichromate is among the most powerful of oxidizing agents and it has extensive uses as such in the practice of chemistry; chromate is a less active compound. This property is very much more in evidence in the presence of acid, and sulphuric acid appears in the formulae for chromium deposition.

A compound is an oxidizing agent because it is itself subject to reduction; hydrogen is a reducing agent, particularly as it is liberated from its compounds. It is present as such in the action shown by the equation above.

Therefore in these favourable conditions the chromate and dichromate radicles are reduced to the metal atoms:

$$8H^+ + CrO_4^- \longrightarrow 4H_2O + Cr \downarrow$$
$$14H^+ + Cr_2O_7^- \longrightarrow 7H_2O + 2Cr \downarrow$$

These equations represent the ideal reaction: it is unlikely that the whole of the chromate–dichromate radicles are simultaneously reduced.

Since the sulphate ion is present—from sulphuric acid and many of the formulae show chromic sulphate ($Cr_2(SO_4)_3$)—the continuing action is probably

$Cr^{+++} + 3$ electrons	$2H_2O + 2SO_4$ (discharged)
$= 3\,Cr$	$2H_2SO_4 + O_2 \uparrow$
Cathode	Anode

Since the anode is a practically inert lead alloy, it is necessary to replenish the electrolyte as the deposition proceeds.

Tin. Tin deposition is employed solely to face the electrotype shells to ensure adhesion of the backing metal; the practice is an alternative to the use of metallic tin or solder with a high tin content.

A salt of tetrafluoroboric acid (HBF_4) is probably the best-known electrolyte for the purpose. Assuming the lower valency, this is stannous fluoroborate—also 'fluoborate' and 'borofluoride' ($Sn(BF_4)_2$)—and it may be supposed to follow the usual course of a salt in electrodeposition:

$Sn(BF_4)_2$	$\xrightarrow[\text{electrolysis}]{}$	Sn^{++} (discharged)	$2BF_4^-$
		$\downarrow$	
		Sn	
Stannous fluoborate		Cathode	Anode

Cleaning and activating of plastic stereos. The formula given for this purpose is an acid–dichromate which is considered above under chromium. This is a very active oxidizing agent which

chemically cleans the plastic surface, and is apparent that it also renders the plastic receptive to the subsequent precipitation of metallic silver.

Sensitizing solution as preparation for silver spray. Stannous chloride ($SnCl_2$) is well known as a reducing agent. It is oxidized readily to the stannic (Sn^{++++}) state. This salt tends to be precipitated in aqueous solution as basic stannous chloride (Sn(OH)Cl) also called oxychloride; the addition of hydrochloric acid prevents the formation of this compound.

The sensitizing action of stannous chloride may be ascribed to its part in the reduction of the silver salt.

Silver spray—reduction of silver nitrate. This is a familiar example of chemical reduction. The most usual reducing agent for this purpose is formaldehyde, but almost any aldehyde would serve. Ammonia is added to the silver nitrate solution to precipitate silver oxide, which then redissolves in excess ammonia:

$$\underset{\text{Ammonium hydroxide}}{NH_4OH} + \underset{\text{Silver nitrate}}{2AgNO_3} = \underset{\text{Silver oxide}}{Ag_2O} + \underset{\text{Nitric acid}}{HNO_3} + \underset{\text{Ammonium nitrate}}{NH_4NO_3}$$

Formaldehyde is a gas and it is generally used in aqueous solution as formalin. Its reducing action is

$$\underset{\text{Formaldehyde}}{HCHO} + \underset{\text{Silver oxide}}{Ag_2O} = \underset{\text{Formic acid}}{HCOOH} + \underset{\text{Silver}}{2Ag}$$

The above represents the essentials of the PIRA process.

Hydrazine (N_2H_4 or $H_2N.NH_2$) is an alternative reducing agent for the silver nitrate. This compound is commonly employed as the sulphate ($N_2H_4:H_2SO_4$) or the hydrate ($N_2H_4.H_2O$), but in the reaction the hydrazine is functional:

$$\underset{\text{Hydrazine}}{N_2H_4} + \underset{\text{Silver oxide}}{2Ag_2O} = \underset{\text{Silver}}{4Ag\downarrow} + \underset{\text{Nitrogen}}{N_2\uparrow} + \underset{\text{Water}}{2H_2O}$$

In the above, ammoniacal silver nitrate giving silver oxide is used; the reducing action is also practicable with silver nitrate:

$$\underset{\text{Hydrazine}}{3N_2H_4} + \underset{\text{Silver nitrate}}{2AgNO_3} = \underset{\text{Silver}}{2Ag\downarrow} + \underset{\text{Nitrogen}}{4N_2\uparrow} + \underset{\text{Water}}{6H_2O}$$

Copper spray. The precipitation of copper is possible by the use of the above reducing agents:

$$\underset{\text{Cupric sulphate}}{CuSO_4} + \underset{\text{Potassium hydroxide}}{2KOH} = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Cupric hydroxide}}{Cu(OH)_2}$$

The addition of Rochelle salt prevents the precipitation of the cupric hydroxide (see under "Copper", p. 296). The whole is Fehling's solution, well-known in analytical chemistry.

$$\underset{\text{Formaldehyde}}{HCHO} + \underset{\text{Cupric hydroxide}}{Cu(OH)_2} = \underset{\text{Copper}}{Cu\downarrow} + \underset{\text{Formic acid}}{HCOOH} + \underset{\text{Water}}{H_2O}$$

The formaldehyde should be highly concentrated.

$$\underset{\text{Hydrazine}}{N_2H_4} + \underset{\text{Cupric sulphate}}{2CuSO_4} = \underset{\text{Copper}}{2Cu\downarrow} + \underset{\text{Nitrogen}}{N_2\uparrow} + \underset{\text{Sulphuric acid}}{2H_2SO_4}$$

A proprietary copper spray is available.

Since precipitation of the metals is rapid, the two solutions are mixed in the spray.

Electrical aspects. Since the electrolytes are fair to good conductors the electrical pressure required is low, rarely exceeding 6 V. However, the considerable energy demanded by electrolysis indicates that ample current must be available.

It should be apparent that direct current (d.c.) is imperative; where the public supply is alternating current (a.c.) adjustment may be effected by means of a step-down transformer and rectifier; with d.c. mains or as an alternative to the former, an electric motor coupled to a low voltage d.c. generator is efficient.

The e.m.f. is varied directly as the distance separating the electrodes and as the resistance of the electrolyte.

Current density is defined as the current (in amperes) for each unit of area of the electrodes; this varies very widely, being determined by the nature of the electrolyte and the character of the required deposit.

As is the case in the majority of chemical reactions, deposition

is accelerated by rising temperature and higher current density is necessary. However, all electrolytes have an individual optimum temperature or temperature range.

Information on the above subjects is given in Table 18.1: it is necessary to observe, however, that variations exist in workshop practice.

TABLE 18.1

Electrolyte (principal component)	Temperature	Current density (amps per 1000 cm²)	EMF (volts) electrode distance 14 cm (5·5 in.)
Cupric sulphate (with H_2SO_4)	18°C (64°F) (room)	50–100	3–4
Cupric sulphate (with H_2SO_4)	38°C (100°F)	100–150	4–6
Cuprous cyanide (flash or strike)	80°C (176°F)	5–10	2·5–3
Nickel sulphate	50°C (122°F)	10–15	4–6
Nickel sulphamate	38°C (100°F)	20–40	6
Chromium trioxide	40°C (104°F)	200	4–6
Stannous fluoborate	18°C (64°F)	50	1–3

Faraday's laws of electrolysis. Faraday's studies in so many fields, including electrolysis, were remarkable; it is even more remarkable that so many of his conclusions remain valid. The principal difference between his and the current views on the subject of the present chapter is that he supposed that the passage of the electricity *caused* the ionization of an electrolyte; it is now accepted that ionization is characteristic of these substances in solution and probably in any state.

The laws of electrolysis are two:

(a) The mass (weight for most purposes) of any substance liberated by the passage of an electric current is directly proportional to the quantity of electricity which has been passed.

(b) The masses of various substances liberated by the passage of the same quantity of electricity are exactly proportional to the chemical equivalent of each.

"Quantity of electricity" is expressed in terms of a fundamental unit—the coulomb—which is defined as that quantity of electricity transferred by 1 ampere during 1 second.

The weight of some of the substances liberated by 1 coulomb during electrolysis and considered in this chapter may be established experimentally—this weight is the electrochemical equivalent of each of these substances; if the chemical equivalent (see Chapter 11, p. 175) is divided by this weight a remarkable uniformity appears (Table 18.2).

TABLE 18.2

Substance	(A) Electrochemical equivalent	(B) Chemical equivalent	$\frac{B}{A}$
Hydrogen	0·0000104	1·008	96,498
Silver	0·001118	107·8	96,495
Copper (Cu^{++})	0·00033	31·79	96,556

(Rather more precise figures have been used for the chemical equivalents than those derived from the table.)

It therefore appears that 96,500 coulombs (a faraday) liberate 1 g equivalent of a substance, and it becomes possible to calculate the amount of a metal deposited in a given time if the quantity of electricity used is known.

To give a simple example. If a steady current of 50 A is passed through a solution of cupric sulphate for 2½ hr the amount of the metal deposited is:

$$\frac{\text{Amps}}{50} \times \frac{\text{Hours}}{2{\cdot}5} \times \frac{\text{Minutes}}{60} \times \frac{\text{Seconds}}{60} \times \frac{\text{ECE copper}}{0{\cdot}00033}$$

i.e. 148·6 g.

CHAPTER 19

The Lithographic Process

Introduction. Lithography is perhaps the least obvious and surely the most complex of the printing methods. The means of ink transfer from an image in relief or intaglio to the paper, if not as simple as might be inferred, is still mechanical and apparent while lithography applies subtle chemical and physical principles which even today are imperfectly understood. The earlier explanations merely state the observed facts: image and non-image zones are essentially flat (hence 'planography'); differences, if any, in relief are incidental; the non-image is water-accepting and consequently oil-refusing while the image is the converse; in brief, oil or grease and water do not mix.

It is perhaps a little surprising that, in spite of the development of the machine, there is little fundamental difference between Senefelder's invention of 1798 and modern offset lithography from metal plates—offset alone excepted.

Lithographic stone. This is the material from which the process derives its name (Greek *lithos* "stone", and *graphos*, "writing"); the word will persist even if the stone disappears for good (or will it be for "good"?). This beautiful material is an oolitic limestone of very fine structure consisting of 93 per cent upwards of calcium carbonate ($CaCO_3$), the remainder being magnesium carbonate with traces of aluminium and iron. 'Oolitic' implies an egg-like structure in miniature; the word is used by geologists to denote a division of the Jurassic system. The stone is, or was, quarried at Solenhofen in Bavaria, not a great distance from Senefelder's home

at Munich and, although it occurs elsewhere, the original source is believed to be supreme.

Preparation of the stone. The stone as quarried is sawn and ground to give parallel back and front faces; the latter is either grained, using sand, or polished to a smooth surface by means of a fine, hard snakestone. The dried stone is now ready to accept an image in greasy ink or crayon applied manually or an ink image by transfer from an engraving. Photographic transfers are possible, and there is a declining practice of direct printing to stone by the methods of the photolithographer—the difficulty being the sheer weight of the stone. There is considerable variation in technique following the imposition of the image. The following summary represents a common practice, the image is given a protective covering of powdered resin and french chalk and the stone is treated with a mixture of dilute nitric acid and gum-arabic. The former imparts a very slight relief and some granularity; the action being

$CaCO_3$	+	$2HNO_3$	=	$Ca(NO_3)_2$	+	H_2O	+	CO_2
Calcium carbonate		Nitric acid		Calcium nitrate		Water		Carbon dioxide

during which the non-image areas are desensitized by the gum.

Absorption and adsorption. Absorption is the taking up into the pores of one substance of another as, for example, the penetration of water into a sponge or blotting paper. Adsorption is defined as a concentration, sometimes high concentration, of a substance on the surface of another. The atoms or ions of a crystal are maintained in definite positions by forces acting between them but at the crystal surface the forces are exerted in one direction only; therefore other atoms, ions, or molecules of suitable substances are attracted by these available forces. Absorbed materials are usually readily removable—the water may be squeezed from a sponge—but an adsorbed solid, liquid, or gas may be held so tenaciously that separation is very difficult.

Adsorption of gum-arabic. In view of the porous nature of the stone some of the gum must be absorbed, but adsorption is the phenomenon to which the desensitization (p. 310) is ascribed; the

gum adsorbed or otherwise, is markedly hygroscopic, and this property is intensified by the aggregation of the particles which, as shown by Dr. G. L. Riddell, reaches a maximum in a highly viscous solution at a pH of 7·6—a little on the alkaline side of neutral.

Metals. The use of metal sheets in place of the cumbrous stone was suggested early in the history of lithography—Senefelder's English patents of 1801 actually covered the use of metal.

Zinc and aluminium are the single metals commonly employed and there is no doubt that others are practicable, but these fulfil the chemical, physical, and mechanical requirements very well. Bi- and tri-metal plates involve the use of one metal for the image and another for the non-image areas (see below); trimetal in this context is rather a misnomer since the third metal is a mechanical support only—its companions function in the lithographic sense.

Graining. It is possible to obtain impressions from a smooth plate and, indeed, some excellent small editions are produced in this manner and several presensitized and bimetal plates are almost grainless. However, grained plates are generally favoured and, while it is possible to obtain a fine grain chemically, abrasion is the normal practice; the character of the grain is determined largely by the composition and particle size of the abrasives. The principal materials are:

Pumice powder: made by crushing air-blown lava; in the light of its origin it is unlikely to be a single compound and it is mainly a complex of aluminium silicates [$Al_2(SiO_3)_3$] with iron, potassium, sodium, calcium, and other metals.

Sand: predominantly silica (SiO_2).

Aluminium oxide (Al_2O_3): prepared artificially for abrasive purposes; it is a very hard refractory material.

Carborundum: silicon carbide (SiC); it is among the hardest known materials.

The operation of graining is carried out in a trough with marbles of glass or steel, the abrasive, and water. The trough is agitated in such a manner that the marbles with the abrasive move over the plate in small more or less concentric circles.

This form of graining is employed by the printing house to recondition used plates, but many of the manufacturers favour

sandblasting in which the abrasive is directed to the dry plate under pressure. Brush graining is said to produce a very fine grain; rotating steel or nylon brushes charged with an abrasive travel over the surface of the plate.

Purpose of graining. It is commonly said that the grained surface retains water or anchors the ink more effectively; this is to state the obvious—the reason for the added efficiency for these purposes is that graining increases the surface area by from four to six times according to the character of the grain.

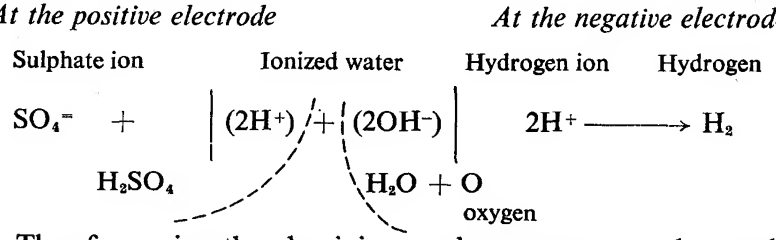
Anodized aluminium. It is well understood that aluminium is readily attacked by oxygen and that the hard continuous layer of aluminium oxide effectively protects the plate from further chemical action; this compound has an aqueous solubility so low that it may not unreasonably be said to be insoluble. With this accepted it is apparent that some means of increasing under control this barrier of aluminium oxide would be of great advantage.

When an electric current is passed through a dilute solution of sulphuric acid a form of decomposition results:

$$\underset{\text{Sulphuric acid}}{H_2SO_4} \xrightarrow[\text{electrolysis}]{} \underset{\text{Sulphate ion}}{SO_4^{=}} + \underset{\text{Hydrogen ion}}{2H^+}$$

The negative acidic radicle moves to the positive electrode (anode); the positive hydrogen ion to the cathode.

The sulphate radicle combines with the hydrogen component of water and oxygen is liberated; the hydrogen ions form molecular hydrogen; the action may be shown as



Therefore using the aluminium under treatment as the anode and an inert cathode such as stainless steel, the liberated and very reactive oxygen forms aluminium oxide, the sulphuric acid is

regenerated, and molecular hydrogen appears at the cathode. (Electrolysis is considered more fully in Chapters 11 and 18, pp. 205 and 294).

The anodized surface will accept dyes since, in spite of its hardness and resistance to chemical action, it is porous; dyed anodized aluminium finds some uses for elegant automobile bodies, and it was widely favoured for hydroplane floats in the Second World War.

The oxide layer has a thickness of the order of 0·005 mm (1/500 in.), and in the lithographic process it serves as a fine grain; however, it is subjected to undisclosed further treatment to reduce the porosity by modifying the structure. It is evident that anodized aluminium approaches more nearly the condition of litho stone than any of the other metals in use in the industry.

Sensitizing or preparation of the metal. Sensitizing in the lithographic context means rendering the metal grease or oil receptive; this practice is not essential for photolithography since the hardened image is held firmly to the metal in any case and therefore this treatment may be deemed to be cleaning or freeing from corrosion. Zinc is usually subjected to the action of dilute nitric acid and an alum; the latter is one of a group of complex compounds consisting of a monovalent metal sulphate with a trivalent metal sulphate and considerable water of crystallization. For this purpose ammonium (or potassium) alum is usually selected. While the action of the acid is obvious (see Chapter 17, p. 287) the effect of the alum is obscure although there is an apparent action—the surface of the metal is given a matt whitish finish; it has been suggested that this is a basic aluminium sulphate—$Al_2(SO_4)_3$. $Al(OH)_3$—which, precipitated on the metal, has much the same function as the oxide layer on the anodized aluminium although it can hardly be as effective. Aluminium is often treated in the same manner, but it is probably more usual to bathe the plate in dilute sulphuric acid sometimes including a dichromate. This treatment has no effect on an anodized plate and little if any on the normal aluminium surface since the substantial oxide layer of the first and the lesser layer of the latter are almost inert chemically, but there will be the removal of unwanted foreign matter.

Photographic images. These are considered in Chapter 16.

Desensitization of the metal. The non-image areas of the plate are made water-receptive in exactly the same manner as is litho stone; the hygroscopic gum-arabic is adsorbed on the plate surface. It is appropriate at this point to observe that, while this gum is the standard, a cellulose derivative, Cellophas (a product of Imperial Chemical Industries), was developed by PIRA as an effective substitute, particularly on zinc. Exudations of trees related to the acacia have been used without marked success.

In normal practice the plate is given a preliminary treatment commonly but inaccurately called etching. These etches in general consist of a phosphate, which hydrolyses to the acid, with a nitrate or phosphoric acid with or without gum. The first type is a salt etch while the latter is considered a corrosive etch. In fact, since the basic radicles of the salt etches are almost invariably ammonium, a very weak base, both types will exhibit a markedly acid pH value. Phosphoric acid (strictly orthophosphoric) is tribasic and, although ammonium dihydrogen phosphate is shown in most of the formulae, it would appear to be of little consequence if the normal or the monohydrogen salts were substituted.

The action of the above salt etch is rather obscure; it may be suggested as

$$\underset{\text{Zinc}}{3Zn} + \underset{\substack{\text{Ammonium}\\\text{dihydrogen}\\\text{phosphate}}}{2NH_4H_2PO_4} + \underset{\substack{\text{Ammonium}\\\text{nitrate}}}{2NH_4NO_3} =$$

$$= \underset{\substack{\text{Zinc ammine}\\\text{phosphate}}}{Zn_3(NH_3)_4(PO_4)_2} + \underset{\substack{\text{Nitric}\\\text{acid}}}{2HNO_3} + \underset{\text{Hydrogen}}{3H_2}$$

This salt etch is generally preferred for zinc. Although it may be used for aluminium a corrosive etch is normal for that metal:

$$\underset{\text{Aluminium}}{2Al} + \underset{\substack{\text{Phosphoric}\\\text{acid}}}{2H_3PO_4} = \underset{\substack{\text{Aluminium}\\\text{phosphate}}}{2AlPO_4} + \underset{\text{Hydrogen}}{3H_2}$$

The complex phosphates or the phosphate are adsorbed at the metal or oxide surface to form a partially hygroscopic layer; the gum-arabic completes the desired action. It is frequently asserted that there is chemical combination between the gum and the metal; in fact there is little or no evidence for this and the influence of the gum is ascribed to the almost wholly physical process of adsorption.

Deep-etch plates. The photographic aspects and the etching of the important deep-etch process are discussed in Chapter 16.

Metals, oil and water. Water falling on a greasy surface is repelled; under the influence of its own surface tension it will form globules which have very little contact with the grease. It is possible to adapt this action to determine the wettability of the metals of lithography, but it is also important to discover the oil-accepting properties of these metals in the presence of water since oily materials and water are used simultaneously in the process.

In experiments conducted by R. A. C. Adams and discussed later by Dr. W. H. Banks (both of PIRA), the metal under examination was immersed in distilled water. A drop of oil was led to the downward face of the metal and when equilibrium was established the tangent of the angle made by the surface of the globule and the plane of the metal was measured, the shape being projected through the water to a screen. It is evident that the greater the angle the lower the affinity of the metal for oil in the presence of water; the converse means that in the unlikely event of the oil flattening out on the metal the contact angle is zero and the affinity total (Fig. 19.1).

The information obtained with an inert oil for some of the familiar metals used in lithography is:

Zinc	Copper	Stainless steel	Aluminium	Chromium
30°	77°	110°	140°	150°

Bimetal plates. It is probable that the character of these metals was known before the results of the experiments since bimetal plates prepared almost 40 years ago used copper for the image and stainless steel for the remainder. In any event it is clear that zinc or copper are the most suitable image bearers with one of the

remaining metals for the rest. There are evidently difficulties in the case of zinc, and in practice copper is all but unchallenged. It is necessary to observe that the performance of any of these metals is likely to depart a little from the ideal since they are influenced by graining (chiefly the single metals) and the various treatments of sensitization and desensitization.

Trimetal plates in this context need not be differentiated since two metals are present for lithographic purposes, the support being either zinc or steel.

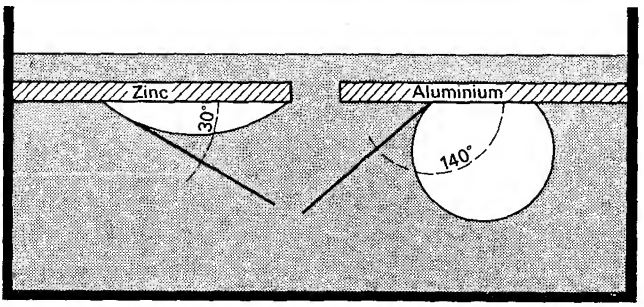


FIG. 19.1. Contact angle.

For plates intended for production from a negative, copper is electrodeposited on stainless steel. The image being laid down in a suitable photoresist, dichromate-PVA for example, the copper on the non-image area is removed to expose the stainless steel; any of the well-known mordants may be, and are, used, the stainless steel being almost inert.

The action of ferric chloride on copper is shown in the chapter on the chemistry of etching; here it is proposed to set down the action of another ferric salt:

$$Fe(NO_3)_3 + Cu = Fe(NO_3)_2 + CuNO_3$$

Ferric nitrate — Copper — Ferrous nitrate — Cuprous nitrate

The majority of the available plates are intended primarily for positive working; these are electrodeposited chromium on sheet copper or deposited chromium on deposited copper with a steel or other support.

The photographic printing to metal exposes a chromium image which must be removed since the underlying copper is to constitute the image. The usual mordant is hydrochloric acid, to which copper is practically inert, with calcium or other chloride added almost to saturation to inhibit attack on the stencil. The action is probably:

$2Cr$	$+$	$6HCl$	$=$	$2CrCl_3$	$+$	$3H_2$
Chromium		Hydrochloric acid		Chromic chloride		Hydrogen

Planography using mercury. Mercury will form an amalgam, a solid solution, with copper while chromium and most other metals do not. It has long been known that mercury–copper amalgam is ink-refusing, and suggestions were made from time to time that it might be the basis of waterless lithography. "Pantone" of A. R. Trist came very near to success, but it was killed by the fear of mercury and the advent of the Second World War. The raw material was chromium plate on copper; an image, halftone or line, preferably in dichromate–albumen, was printed from a negative and the exposed non-image chromium was removed by hydrochloric acid as in the paragraph above. The photoresist was removed to expose the chromium and the plate treated with mercury to form the amalgam. Printing was possible on both litho and letterpress machines, a small amount of mercury being added to the ink. The results were excellent and there is little doubt that Pantone, or something like it, will be revived or invented.

Dry offset lithography. This may be defined as the printing from plates etched into low relief on offset-litho machines. It is certainly *not* lithography and "letterset" is worse.

Electrostatic processes. A number of processes have been developed, chiefly for the duplication of commercial documents, which apply static electricity and photoconductivity. The best known is Xerography (Rank-Xerox). This subject is considered in the section devoted to electrostatics of Chapter 8 (pp. 96–98).

Part V

Fundamental Materials

CHAPTER 20

Paper and Board

Introduction. Apart from stone slabs, rock faces, and clay, many more or less flexible materials were used for drawing and writing before the invention of paper. These included various textiles and parchment prepared from animal skins, but the most valuable of all the predecessors of paper was made from the papyrus, a reed still abundant by the Nile. The reeds were unrolled and laid on flat stone side by side; other layers were added, after gumming, with the grain at right angles to the first and the process repeated as required. The use of prepared papyrus is believed to have originated earlier than 3000 B.C. and it was well known beyond its country of origin; it is likely that most of the works of the authors of classic antiquity were inscribed on papyrus and it survived in Egypt until about A.D. 1000. Its name endures, since our "paper" and almost similar words in many other languages are obviously derived from that of this plant.

Once again China claims attention; it is held that there is good evidence that one named Tsai Lun invented papermaking around the year A.D. 105, and it is further believed that the process was almost identical with that in use today for handmade paper.

Papermaking spread to central Asia, and the art was quickly acquired by the Moslems of Samarkand and Bokhara to be carried by the still triumphant Arabs across North Africa into Spain by about 1150; as knowledge grew the process was established in France, Germany, Switzerland, and Italy to reach

the Netherlands about 1400. Paper was first made in England in 1490 and in the English colonies in North America in 1690.

The raw materials of paper. Paper may be defined as the product of intermeshed—in distinction to woven—vegetable fibres. It has been stated that any of these fibres which will float are suitable for papermaking and, in fact, a great variety of such materials is in use for the purpose.

The most important of the early materials were linen and cotton rags, but with the expansion of printing from the eighteenth century onwards the discovery of other sources became imperative. Straw was found to be effective and fairly abundant but the search continued. The first "mechanical wood" or "groundwood" pulp was manufactured in Germany in 1844, and a patent was granted in England in 1854 for "chemical wood" pulp made by treating the raw material with caustic soda. Esparto, commonly called a grass, is strictly the leaf fibre of a plant which flourishes in the semi-arid parts of North Africa and Mediterranean Spain. Its use for papermaking developed rather slowly during the second half of the last century, but it is now among the most important of the sources of paper.

Cellulose. Whatever the vegetable origin, ideally all the fibres of papermaking are chemically cellulose, a substance which forms the greater part of the structure of plants. Cellulose is a carbohydrate closely related to starch and the sugars with the empirical formula $(C_6H_{10}O_5)_n$. For further consideration of this subject the reader is referred to Chapter 12. Here it may be stated that carbohydrate means a substance which appears to be constructed of carbon and water and that the n signifies any number of the units within the brackets. In the case of cellulose the unit is repeated from 3000 to 10000 times, and thus the molecule is very large.

Other substances likely to be present are lignin, particularly in wood pulps, different carbohydrates and gums according to the plants of origin.

Raw cotton-wool contains about 90 per cent of pure cellulose with 8 or 9 per cent water, the residue being very small amounts of wax, resin, and mineral matter; thus papers made from cotton (filter papers for example) are practically cellulose only, the other

substances having been removed in the process of manufacture. Conversely, the untreated fibres of many woods used for papermaking contain only from about 40 to 55 per cent of cellulose, much of the remainder being the deleterious lignin which is removed as far as possible with due regard to the economics of the papermaking process.

Mineral and other additives. While the definition of paper remains valid and cellulose is accepted as the basic material, other substances may be added during and at the end of the papermaking process. Fillings or loadings, mainly of mineral origin such as kaolin (or china clay) and titanium dioxide, are used to increase opacity and give body often at the expense of mechanical strength. Surface sizing is the coating, with more or less adhesive substances such as starch, to cement the surface fibres and reduce fluffing. In coating in the full sense a layer of china clay and barium sulphate with casein or gelatin is added to give the hard and even polished surface preferred for high quality halftone in letterpress and litho printing.

Paper testing. Papermaking is an ancient industry and consequently there are very many valuable tests of the product derived from accumulated observation and experience. All that tests based on the physical sciences can add are certain quantitative or numerical aspects which are largely outside the scope of observation. In the matter below the tests are divided into three groups which may be regarded as rather arbitrary, particularly in the case of the first two.

(a) Mechanical Tests

Substance. This is defined as the weight of a stated area of paper and it should be determined by examination of a fully air-conditioned sample only. The future standard will surely be the weight of a square metre expressed in grams (or kg) which is largely accepted on the Continent already. In the meantime, substance is still given in the United Kingdom in terms of the weight of paper of the stated dimension to the ream of 480, 500, or 516 sheets.

Substance may be assessed by the use of a chemical balance to

weigh a definite fraction of the given sheet and thus to obtain that of the whole sheet and the ream by multiplication. This somewhat cumbrous procedure may be avoided by the use of the quadrant balance in which a sheet is inserted in the wire container and the weight of a ream read off on the scale when equilibrium is reached. A similar balance is employed to determine substance in grams per square metre. A template is used to cut a 10 by 10 cm piece of

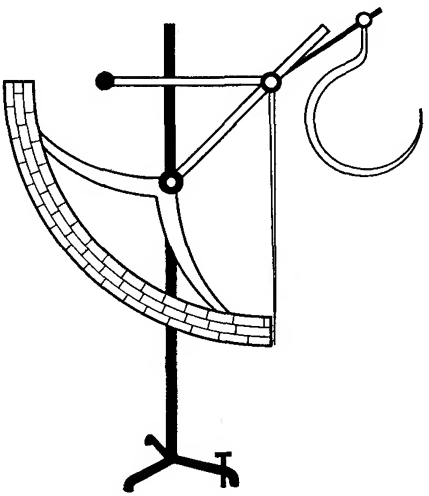


FIG. 20.1. The quadrant balance (Messmer).

the sample; this is suspended by a corner on a slender hook and the weight in the stated terms appears on the scale (Fig. 20.1).

Substance of board. While board is largely used for a variety of purposes for which paper is unsuitable, in this chapter, in general, the considerations applied to paper also apply to board, but the latter does differ obviously from paper in substance.

Board is defined as having a substance of not less than 220 g/m² or 90 lb to the 480-sheet ream, each sheet being 20 by 30 in.

Calliper. This means thickness and it is determined very easily by use of the deadweight dial micrometer; the standard eight

sheets are inserted between the raised jaws of the clamp and the control lever slowly lowered into contact. The total thickness of the eight sheets is shown in microns (1/1000 mm) or thousandths of an inch and that of a single sheet obtained by division. It is desirable to conduct not less than ten tests in different parts of the sheets and express the result as the average.

Bursting strength. While there are a number of machines for this test, all function in much the same manner; a sample of the paper is rigidly held at its edges by a ring and a flexible rubber ball is slowly forced into the paper by the manual rotation of the handle. The increasing pressure, expressed in ounces per square inch or grams per square centimetre, is shown on the gauge; when the sample finally gives way the pointer remains in position.

Tensile strength. A strip of paper is gripped at both ends and tension on the free end gradually increased until the paper breaks, the point at which this occurs being indicated on the dial. The standard dimensions of the paper under test are 16 mm wide by 18 cm, but since the latter is the size within the grippers the paper must be rather longer. Further, the test should be conducted in both directions since the tensile strength is almost certain to vary in this sense.

(b) Physical Tests

Surface oil absorption. The rapidity with which the vehicle, an oil, is absorbed by the paper, has a great influence upon the quality of the impression, particularly in letterpress and lithographic printing. If the oil remains too long on the surface, setting of the ink will be prolonged while, in the contrary case, if the oil is taken in too quickly, the pigment and other more less solid components will be left on the surface with little or nothing to bind them, and powdering is the result.

The PIRA apparatus is the most successful yet evolved for this difficult determination of oil absorbency. A heavy brass or gunmetal cylinder is retained at the higher end of an offset blanket-covered incline. A small piece of the sample is placed towards the lower end with its centre about one and a half diameters of the

cylinder distant from the top. A drop of paraffin is allowed to fall on the cylinder and the latter released; at a half revolution part of the oil is deposited on the blanket and with a further revolution some of the remaining paraffin is deposited on the sample. The paper is quickly withdrawn and viewed obliquely; the sequence from deposit of the oil to the disappearance of the gloss, indicating absorption of the greater part of the oil, is timed by a stop-clock. The average of a number of tests is necessary in the interests of accuracy since a single observation is hardly likely to be acceptable.

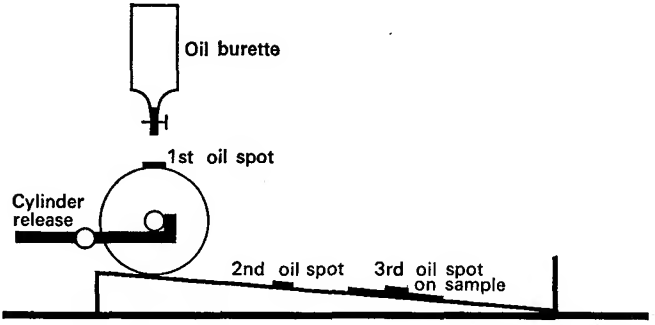


FIG. 20.2. Diagram to illustrate oil absorbtion test (PIRA).

For coated papers about 10 sec should be the minimum oil absorption time to limit the risk of powdering, while the maximum should be from about 150 sec to 200 sec (Fig. 20.2).

Moisture content or absorbency. This test may be used to assess the water content of the sample in the existing humidity conditions or to assess the avidity of the sample for water. For the former the paper is taken after normal conditioning, while for the latter it is exposed at least an hour close to a large dish of water. A small cylindrical glass vessel with a well-fitting stopper is dried, cooled, and weighed; a gram, or about a gram, of the sample is placed in the vessel and the whole weighed again; the paper should either be shredded or very loosely folded. The difference in weight gives an accurate weight of the paper sample. The unstoppered vessel

and sample are placed in an air oven maintained at a temperature of 105°C for 1 hr; the vessel is withdrawn (with care), the stopper replaced quickly, and the whole cooled, preferably in a desiccator, and weighed. The loss in weight obtained after subtraction of the last weight from that of the combined original sample and vessel gives the weight of the expelled water.

The calculation is

$$\frac{\text{Weight of water}}{\text{Weight of original sample}} \times 100$$

(the result being expressed as percentage); if a gram of the paper is taken, the calculation becomes much simplified.

Moisure stretch. It is essential for critical register work that the paper should be conditioned to the relative humidity of the machine room. The paper may be tested simply by taking a sheet from the centre of the package, quickly marking a line 1 m or 3 ft in length, using a steel rule, and exposing the sheet freely to the air of the room for about 20 min. Remeasurement will indicate (a) stability or equilibrium, (b) expansion, or (c) contraction, the first being evidence of correct conditioning, the second that water has been taken in while the last means that the paper has lost moisture. Dimensional instability with changes in relative humidity is very much more apparent across the machine direction of the paper.

The PIRA Paper Equilibrium Tester functions in much the same manner as that described; it is a steel blade which is inserted into the package and which imposes widely separated marks. The variation in size, if any, is checked after exposure of the paper through two apertures spaced exactly as the original marks.

Opacity. A material which transmits no light is said to be opaque. For the present purpose opacity may be defined as the extent to which a material approaches the opaque. No paper is completely opaque but its opacity is among the most important criteria of its quality since much, or even any, show-through is evidence of an inferior material.

Opacity may be assessed by the use of diffuse white integrating chamber with a photocell connected with a galvanometer and a

removable head which is a dull black cavity. The test is carried out by folding some of the sample sufficiently for the whole to be considered opaque; the folded paper is placed under the head which completely light-seals the chamber. The infinitely reflected light within the system is received by the photocell and recorded on the galvanometer. The latter is set at 100 per cent. A single piece of the sample is then inserted and some of the light on its

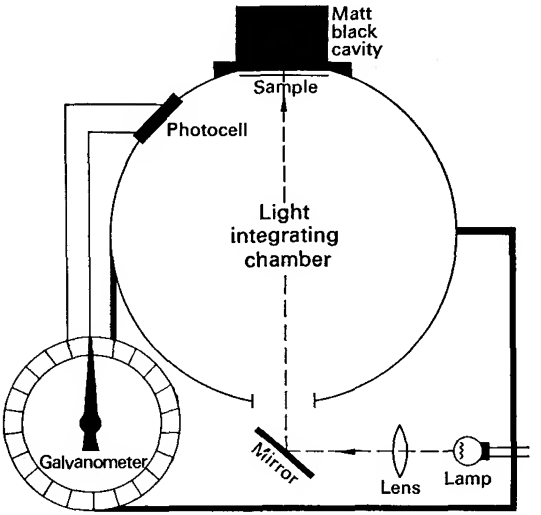


FIG. 20.3. Outline of an opacimeter (after EEL with acknowledgements).

surface is transmitted and absorbed by the black of the cavity. Thus the total light within the chamber is reduced and the reduction registers on the galvanometer as percentage opacity (Fig. 20.3).

Smoothness. The surface texture of paper may be examined under a microscope, preferably binocular, using a shielded illuminant at a very low angle in order to leave shadows in the depressions. The contours may be seen more easily and even exaggerated by rubbing in a soft ink and quickly removing it from the higher levels by wiping.

Gloss. Specular reflection is regular while diffuse reflection appears to be random; in both, the laws of reflection are valid (see Chapter 9), but only the former can be measured precisely as reflection. A mirror provides the best example of specular reflection; that of a rough, uncoated paper is diffuse. The reflection of a coated paper has a specular component which increases with the gloss.

A glossmeter consists of a lamp in a tube with an optical system designed to give nearly parallel rays of light together with another tube containing a photocell the output of which is led to a galvanometer. The tubes are directed towards the base at opposed

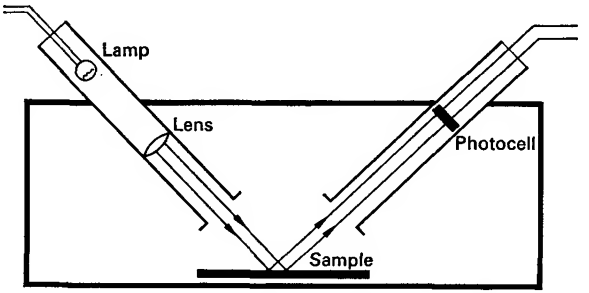


FIG. 20.4. A glossmeter.

angles of 45°; other acute angles would serve but that stated is convenient. In use a reference standard, as in many other cases, is needed; here this is a black glazed tile or, for preference, good glass with the back face painted with a matt black. The reference is placed in the instrument and the galvanometer adjusted to show 100 per cent; the sample is then substituted and its gloss indicated as a much lower percentage (Fig. 20.4).

Whiteness. This quality is of the greatest importance in four-colour printing by any process. If, for example, the paper has a marked yellow component, this colour is added to that already present in the appropriate plate with disastrous results to the accuracy of the colour rendering.

Whiteness may be assessed by means of a reflection densitometer when the sample is referred to a standard white, usually magnesium oxide; this, however, will only indicate the difference in reflectance without giving any information on the actual quality of the white. The most valuable instrument for the purpose is the spectrophotometer (see Chapter 8). Spectrophotometric curves of almost all normal or natural whites show that these tend to be slightly yellow since the blue proportion is depressed (Fig. 20.5); this, indeed, applies to most papers described as white. It is for this

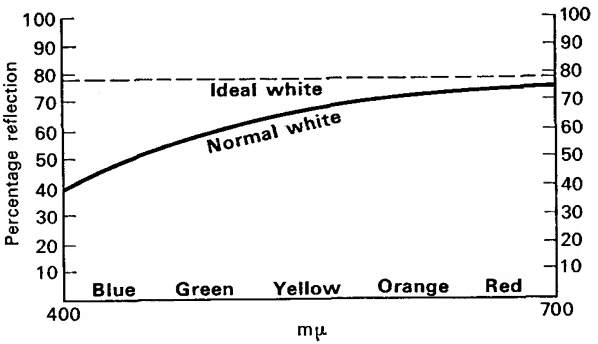


FIG. 20.5. Approximate spectral curve of whites.

reason that a blue component, often fluorescent, is added to washing powders (detergents) with the consequence that "whiter than white" has some meaning.

Recognition of fibres. Paper fibres from their many sources have characteristics which assist in their identification; these are chiefly the dimensions and form of the fibres together with chemical tests. During the manufacturing process fibrillation occurs in which the minute components of the fibres, the fibrils, may be broken away although, in general, the fibres are surprisingly tenacious.

For examination of the fibres a microscope with a magnification from 60 to 80 diameters is suitable; the fibrils would need much greater power to be seriously inspected. The size may be estimated

by the unaided vision or by the use of a very low-powered microscope.

Recognition is further advanced by the employment of the Herzberg reagent which gives distinctive colours to the fibres. The reagent may be obtained commercially or it may be prepared:

(a) A saturated aqueous solution of zinc chloride.
(b) Iodine 0·25 g; potassium iodide 5·0 g; water 12·5 g.

The solutions are mixed before use in approximately equal quantities to the small volumes required.

It is necessary to separate the individual fibres by well soaking a portion of the sample and using needles in wooden handles or similar dissecting implements; a few of the detached fibres are carefully placed on a microscope slide, the surplus water removed from the edges with filter paper, and a drop of the reagent applied. It is rarely really necessary to use a cover-glass but there is no objection to its use.

Table 20.1 gives information on some of the more familiar materials; it is, however, desirable to add that efficiency in these tests is only acquired after much experience.

(c) Chemical Tests

Starch. This may be present on the surface of a paper and its presence must be considered as among the easiest to establish chemically. A very weak solution of iodine in potassium iodide is prepared; weak in order that the colour of the iodine itself should not be apparent. A suitable formula is: iodine 0·10 g; potassium iodide 1·0 g; water 100 ml.

A spot of this solution is placed on the sample by means of a glass rod. A blue or deep blue colour is evidence of starch. This is among the most sensitive of chemical tests; it is said that 1 part of iodine per 1,000,000 is detectable; this is the converse, of course, of the paper test.

Ash content. The residue, after the complete combustion of the cellulose and other organic materials of the sample, may be accepted as the wholly irreducible mineral content added as loadings or coatings.

TABLE 20.1

Source	Type	Size		Form	Herzberg colour
		Length (mm)	Width (mm)		
Cotton plant	Seed hair	30·0	0·025	Flat twisted tube	Red
Flax	Fibre of stem (linen)	22·0	0·02	Pointed at ends. Cross markings	Red
Pine	Wood fibre	3·5	0·03	Thin ribbons with pores	Pale blue (Chemical wood)
Spruce		3·5	0·03		
Hardwoods		1·5	0·02		Yellow (mechanical wood)
Esparto	Leaf fibre	1·5	0·013	Round section. Thick walls Pointed at ends	Violet-blue
Straw	Cereal	1·5	0·015	Tubular Thick walls	Blue

The method is as follows: weigh a dried crucible and lid, add 1 g of the sample to the crucible (the paper may be folded or shredded) and ignite, using a tripod, fireclay triangle, and bunsen, continuing the action until white ash only remains. The lid is used in the final stages to retain the ash. The crucible, lid, and contents are cooled in a desiccator and the whole weighed. The weight of the ash is obtained by subtraction and, since a gram of paper was taken, this in centigrams is also a percentage as is normally required.

Mechanical wood. Lignin, with cellulose, is a principal constituent of wood varying but little with the source. The precise composi-

tion of this material does not appear to have been established; it is, however, of high molecular weight and it has some affinity to cellulose.

In the process of manufacture of mechanical wood, or groundwood, it is inevitable that the greater part, if not, indeed, the whole, of the lignin is retained while, using the same raw material, the treatment with sodium hydroxide, calcium bisulphite, or other compounds removes most of the lignin from the product, chemical wood.

Mechanical wood, by reason of its lignin content, may be detected by several methods, two of which are discussed here.

(a) *Phloroglucinol.* This compound, properly 1,3,5-trihydroxy benzene, is closely related to the photographic developer pyrogallol. The formula is: 2 g phloroglucinol; 50 ml ethyl alcohol; 25 g hydrochloric acid. In the test, a drop of this reagent is applied to the paper by means of a glass rod; an immediate red coloration is evidence of mechanical wood. The very small amount, 5 per cent or less, of any residual lignin of chemical wood is detectable in the same manner, but a microscope is necessary.

(b) *Aniline sulphate*, prepared to the formula 1 g aniline sulphate, 50 ml water, 1 drop sulphuric acid, provides a test of similar type giving an intense yellow coloration which may need a few moments to develop.

It is apposite to mention that the various colours given by the Herzberg reagent are mainly due to the presence of lignin. The red shown by the almost pure cellulose of cotton derived papers represents the basic reaction of iodine with cellulose.

Sulphur. Zinc sulphide and a mixture of this compound with barium sulphate (known as lithopone) are among the loading materials of paper and board; lithopone is also used in paint as a substitute for white lead.

The sulphur of the zinc salt is often described as reducible, which merely means that in appropriate conditions it is released (see Chapter 11 under "Oxidation and reduction", p. 188) and may combine with other basic radicles. Bronze powder and gold inks contain metallic copper and brass which readily form cupric

sulphide (CuS) with sulphur; this is a dull black and it is responsible for the tarnishing of these copper-bearing materials.

The presence of sulphur in paper, even in small amounts, may be shown by heating about 1 g of the suspected sample in a flask with a weak acid such as phosphoric (about 10 ml) in about 20 ml of water or about 2 ml of a mineral acid in the same volume; a piece of filter paper soaked in lead acetate solution will be blackened by the liberated hydrogen sulphide formed if the test is positive. The reactions are (assuming sulphuric acid as a simple example):

$$\underset{\text{Zinc sulphide}}{ZnS} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Hydrogen sulphide}}{H_2S}$$

$$\underset{\text{Hydrogen sulphide}}{H_2S} + \underset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} = \underset{\text{Lead sulphide}}{PbS} + \underset{\text{Acetic acid}}{2CH_3COOH}$$

(Lead sulphide is the black compound; the formula of acetic acid is that conventional for an organic acid).

pH of paper. The printing properties of a paper largely rest upon its acidity or alkalinity; it may appear paradoxical that the pH of a solid is considered at all but, as should be apparent from some of the matter above, paper is very hygroscopic, i.e. water-accepting, and many compounds are used in the manufacture, or are part of the make-up of paper.

The pH of uncoated papers as shown by the hot extraction method (see p. 331) ranges from the considerably acid at 4·0 to the weakly acid at rather above 6·0. With coated papers the paper itself is probably close to these values, but the coating tends to be alkaline at a little above pH 7 to reach as much as pH 9 which should not be surprising in view of the materials.

It has been shown by PIRA and the Lithographic Technical Foundation of the United States that two major influences upon the setting time of letterpress and lithographic inks are the relative humidity (RH) of the machine room and the pH of the paper; the effects may be stated: *drying time increases inversely*

as pH and directly as RH. Both of these influences are present simultaneously and the extract in Table 20.2 of matter due to PIRA makes these effects apparent.

TABLE 20.2

pH of paper	Time of drying in hours	
	RH 65%	RH 75%
6·9	6·6	14·0
5·5	6·7	23·0
4·7	7·6	60·0

It would appear that these experiments were undertaken with a somewhat abnormal ink, but this may be ignored since the same ink was used throughout. However, it is important to note that the retarding effect of the higher RH is most marked at the lower pH values, and thus the latter is actually the greater influence.

Table 20.2 refers to letterpress; in lithography, since the RH tends to be higher on account of the water essential to the process, the control exercised on pH values is of even greater importance. The papers studied in the experiments were uncoated; with coated materials there are other influences, particularly the composition and quality of the coating but work at PIRA indicates that the pH of the coating, independently of that of the paper, should not be less than about 6·5—almost neutral.

The hot extraction method is generally favoured; it is outlined below:

(a) Weigh and shred 1 g of the sample.
(b) Place the paper in a conical flask with 70 ml water.
(c) Insert a reflux condenser in the flask.
(d) Place flask in beaker of water maintained at 98°C for 1 hr.
(e) Cool and decant liquid.

(A reflux condenser in its simplest form is a vertical glass tube carried into the top of the vessel through a water-tight seal; its object is to condense the rising water vapour and return it to the vessel.)

The liquid is tested by any of the methods given in Chapter 13 —paper, liquid, and BDH comparator or Lovibond kit, or electric pH meter—in ascending order of accuracy.

A rapid test of low accuracy is possible. The paper is smeared with an indicator covering the suspected range and the colour change matched against the appropriate Lovibond filter strips.

pH of coating. This is a difficult test but it may be carried out with moderate accuracy as follows. Soak 1 g of the sample in 15 ml of tepid water for 30 min; scrape away the coating into the water as completely as possible; heat the water to boiling, allow to cool and the sediment to settle. Decant the liquid and test for pH by one of the methods above. The pH of the paper itself may, of course, be tested by the hot extraction method as given above.

Paper tests in general. Very many tests have been outlined; there are many others of greater sophistication. Indeed, and very properly, paper heads the test tables.

CHAPTER 21

Ink

Introduction. Printing inks vary widely in type, chiefly in reference to the printing process in which they are used, but in all cases there are two essential components—pigments and carriers or vehicles for the pigments. There are other constituents of a rather lower degree of importance; these are, or may be, substances to promote or accelerate the drying or setting of the ink, solvents, extenders, and materials to bind the pigments on the paper surface.

The inks also differ physically; they range from an undoubted liquid to an apparent solid; again, according to the demands of the process and more particularly to the speed of printing.

The reader is referred for further information on some of the matters below to other parts of this book and specifically to the introduction to organic chemistry (Chapter 13) and to that on the properties of liquids (Chapter 6).

Drying or setting. Drying in this context must be understood to mean much not implied in ordinary usage, i.e. it does not merely indicate evaporation although this is important in more than one class of ink, while even more so it does not necessarily mean the removal of water by this action. For most inks in the major processes, 'setting' is a more appropriate term. The mechanism of setting falls conveniently into four groups of which at least three may occur together. These are:

(a) *Evaporation.* The removal of a liquid vehicle or part of a vehicle by the transition from liquid to vapour phase. The liquid

is normally of low boiling point and evaporation is often accelerated by heat after impression.

(b) *Absorption.* Most papers are very absorbent; this is evident in their avidity for water. They are therefore able to accept the liquid components of the ink to a greater or lesser extent; here it is necessary to stress that all the vehicles are by definition liquids.

(c) *Polymerization.* This is by far the most important of the setting mechanisms, notably in the inks for letterpress and lithographic printing. Polymerization is the formation of very large molecules from the initially simpler structures of the vehicles; it is preceded in most cases by partial oxidation.

(d) *Precipitation.* This may actually occur, in effect, as a fault on some excessively absorbent papers when the vehicle is removed too rapidly to leave the pigment as a powder on the surface. It is specifically employed in a variant of the standard letterpress ink, when, by the introduction of, or contact with, water a component of the ink is detached from its vehicle, carrying the pigment with it.

THE INKS OF THE PRINTING PROCESSES

Intaglio. Copper- and steel-plate inks range from those of the rather low viscosity used for power flat-bed intaglio to those of high viscosity necessary for hand press work on artists' etchings; in composition these inks do not differ widely from those of letterpress and lithography, but it is clearly essential that they are freely removable from the metal surface.

The ground and tablets of cheques are printed in a water-soluble ink to make them secure against alteration and erasure.

These inks are water-based dyes with glycerol or other higher alcohols to raise the viscosity; they set primarily by absorption and evaporation.

Both the intaglio and relief processes are in use for this purpose.

However, by far the greater part of intaglio printing is rotogravure, and here the character of the image surface and the high speed of printing demand an ink of low viscosity; thus gravure ink consists of pigment carried in a volatile solvent and a small

quantity of a resin, soluble in the solvent, to bind the pigment to the paper after the evaporation of the liquid.

Relief. The very high speeds of newspaper printing from rotary stereos and the nature of newsprint make really fluid inks essential, and consequently these inks are made up of a black pigment with a soluble dye (see below) carried in a thin mineral oil. Drying is wholly by absorption except for evaporation of paraffin or similar liquids sometimes added in small quantities to accelerate absorption.

In the other forms of letterpress printing the inks consists almost invariably of a vehicle, boiled linseed, or other natural drying oils and/or synthetic substitutes, driers which catalyse or promote polymerization, and the pigments. The inks may also contain extenders to give body, improve the flow properties, and maintain the suspension of the heavier pigments, and thinners which are usually volatile liquids added also to assist flow and distribution.

Quick-set inks differ from the standard letterpress materials in that the vehicle is modified; it consists of two parts, one more viscous than normal while the other is of sufficiently low viscosity to be described as a thin oil. In use, the latter is quickly absorbed and while with the other component the processes of oxidation proceed in the normal manner, the residual vehicle is dense enough to counter set-off and the other difficulties of rapid printing.

Standard letterpress and other inks when used for food packaging may contaminate the contents since they have very obvious odours. Moisture-set inks are devised to overcome this disadvantage. The vehicles of these inks belong to the glycol series, a group of compounds which accept certain resins and pigments but which release these additions in the presence of excess water; the latter may be that absorbed by the paper or it may be provided by steam directed towards the impression.

Rubber or plastic rollers are necessary with these inks since the usual gelatin composition rollers always retain some moisture; again, these inks are impracticable in lithographic printing on account of the presence of water.

The image surface of flexography is a rubber stereo, or a similar synthetic material may be used; some inks for this variation of relief

printing consist of intense dyes in a volatile solvent together with a resin binder and tannic acid intended to fix or waterproof the dyes. The original dyes for this process were aniline derivatives, and thus flexography is often called aniline printing although many of the materials now in use are not of this type.

The process is particularly valuable for printing on sheet plastics and impervious papers and the inks for these have been subjected to continuous improvement.

Planography. Lithographic inks do not differ in principle from those of the standard letterpress type considered above. However, in view of the essential water, the pigments must be completely unaffected by moisture and, since offset is dominant, the density of the colour must be related to the fact that the ink film on the paper seldom has a thickness greater than 2 μ, i.e. 2/1000 mm.

Screen process. There is considerable variety in the inks, often referred to as paints, for this process. While some of these materials are close in formulation to letterpress inks, the pigments must be exceptionally finely ground to penetrate freely the mesh of the stencil support. Cellulose compounds, often with dyes rather than pigments, in volatile solvents which are indeed very close to paints are widely in use; it is also possible, given a stencil not influenced by water, to employ water-colour inks and water-carried oil-bound materials very like distemper.

MATERIALS OF PRINTING INKS

Until the almost recent past, the components of the inks were few, and apart perhaps from some of the pigments, the majority had been tested by very long use; the properties of these materials seemed to meet the needs of the industry admirably until the demon Progress entered.

Largely during the present century the invention of new processes and the drastic modification of the standard methods made necessary by the increasing appetite of the public for illustration, particularly in colour, accelerated the search for materials adapted to the changing conditions; this search and research are, of course, not peculiar to printing.

In the matter below a selection of the available materials is given; it cannot, within the limits imposed by this work, be regarded as comprehensive.

Vehicles

(i) **Solvents.** These liquids have a dual function; they act as carriers in the inks of some of the printing processes and while their volatility ensures the rapid drying of these inks, the same property is in evidence when they are used as thinners elsewhere.

(a) *Aromatic hydrocarbons.* These are benzene and benzene derivatives. Benzene itself is not used as a carrier or solvent for the purposes under discussion on account of its low boiling point and its low flash point. The latter is defined as the minimum temperature at which the vapour of the substance will ignite when a spark or small flame is applied. The flash point of benzene is below the room temperature of 18° C and in consequence some of its derivatives with higher boiling and flash points are employed (Table 21.1).

TABLE 21.1

Substance	Formula	Systematic name	Melting point	Boiling point
Benzene (benzol)	C_6H_6	—	5·4°C	80·4°C
Toluene (toluol)	$C_6H_5CH_3$	Methylbenzene	− 98·0°C	110·0°C
Xylene (xylol)	$C_6H_4(CH_3)_2$	Dimethylbenzene	− 54·0°C	140·0°C

There are three isomeric xylenes; the information given is that for the meta compound.

(b) *Simple alcohols.* The monohydric alcohols contain one hydroxyl (OH) group (see Table 13.6, p. 229).

(c) *Ketones.* The only member of this group of compounds likely to be encountered in this context is that given in Table 21.2.

TABLE 21.2

Substance	Formula	Melting point	Boiling point
Acetone	CH_3COCH_3	− 94·0°C	57·5°C

(d) *Esters.* This very important class of compounds presents some analogies with inorganic salts; the best known esters for the purpose under consideration are acetates of the lower alcohols (Table 21.3).

TABLE 21.3

Substance	Formula	Boiling point
Ethyl acetate	$CH_3COOCH_2CH_3$	77·0°C
Butyl acetate	$CH_3COO(CH_2)_3CH_3$	127·0°C
Amyl acetate	$CH_3COO(CH_2)_4CH_3$	148·0°C

(ii) **Oils.** These may be hydrocarbons such as light lubricating oils or the natural drying oils of vegetable origin which are very different in chemical composition.

(a) *Mineral oil.* This is normally a mixture of thin oily members of the paraffin series which may be shown as C_nH_{2n+2}, where n stands for numbers from about 14 to 16. The mineral oil used in news ink is very similar to the paraffin used in lamps, but the smelly impurities of the latter are not present.

(b) *Natural drying oils.* These are all natural products in which at least one of the components is "unsaturated" (see p. 219); this property enables these oils to accept air oxygen followed by polymerization during which the liquid tends to become a solid in appearance. None of these oils are single substances.

The obvious example of these oils is linseed, which remains the most widely used and understood of the group. Chemically

it consists of the glycerol esters of at least five of the higher fatty acids, three of which are unsaturated.

To illustrate both unsaturation and fatty acid for this purpose, the formula of linoleic acid is given; this acid is probably the most important of those of the esters of linseed oil:

$$CH_3(CH_2)_4CH = CHCH_2CH = CH(CH_2)_7COOH$$

The double lines in this formidable formula indicate the points of unsaturation at which the process of oxidation and polymerization is initiated.

The companion unsaturated acids, chiefly linolenic and oleic, are very similar to that shown, while in the saturated acids the double bonds do not exist.

The raw linseed oil as obtained from pressing flax seed has a viscosity too low for use; it thickens slowly on exposure, but the process is accelerated by heating to about 200° C in the presence of catalysts. The increase in viscosity indicates a stage of polymerization which will later be continued in the ink.

There are many other natural oils which are used as partial substitutes for the above; these include soya bean, tung, safflower seed, perilla, and sunflower seed oils. All of these oils are chemically close to linseed although specific properties are claimed for each.

Driers. The drying oils set too slowly for most purposes, and various metallic compounds are added to accelerate the action. These are salts of the higher fatty acids with lead, cobalt, and manganese; as, for example, lead, combined with the acid the formula of which is shown above, gives lead linoleate.

These salts are chemically catalysts, i.e. they are substances which promote or accelerate a chemical reaction without undergoing a final change in composition themselves. The precise mechanism by which these substances initiate the oxidation and polymerization of the oil is not completely known as is the case with many catalytic processes.

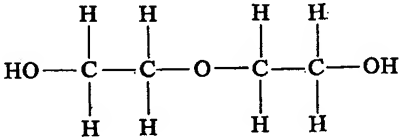
Natural resins. The most important of these additives to some printing inks is rosin, which is the residue from the steam distillation of turpentine—the exudation of many coniferous trees.

The principal constituent of rosin is abietic acid with the empirical formula $C_{19}H_{29}COOH$.

The alkali salts of this acid have some of the properties of soap and thus rosin, also known as colophony, is used in many processes of soap manufacture.

Other natural resins are gum-damar and gum-copal, which are also exuded from several closely related tropical and sub-tropical trees. The use of the word "gum", while justified by time, is actually a misnomer since these substances are certainly resins by definition and very different to the true gums.

Diglycols. These are a class of compound which function both as an alcohol and as an ether; in the latter capacity they act as solvents for substances such as the resins, both natural and synthetic, which are insoluble in water but as lower alcohols they are miscible in and accept water. Therefore in the moisture-set inks the resins initially in solution are precipitated on contact with water. The structural formula of a typical compound is



The two hydroxyl radicles indicate a dihydric alcohol while the oxygen atom joined to two carbons is characteristic of an ether. The compound shown is the ether of diethylene glycol which is also known as a member of the carbitol group.

Cellulose compounds. The most important of these substances are prepared by the action of nitric acid upon the complex carbohydrate, cellulose, and by treating this compound with acetic acid anhydride. The first process gives the nitrate and the latter the acetate both of which are soluble in many organic liquids, amyl esters and acetone among them. The nitrate with a solvent to suit the purpose with resins and other additives is well known in screen process inks.

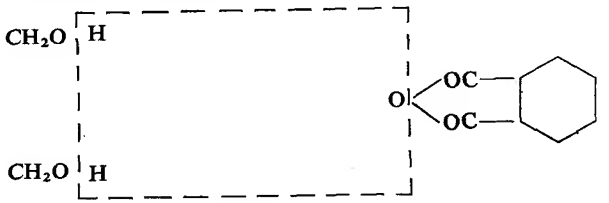
Extenders. While these materials appear at first sight to be adulterants they have, in fact, the serious functions which are

suggested in the introduction to this chapter. There are many extenders in use, principally barytes or *blanc fixe*, both $BaSO_4$ with differences in texture and manufacture, whiting and precipitated chalk, $CaCO_3$ and china clay, a complex aluminium silicate with the probable formula $Al_2O_3.2SiO_2(H_2O)_n$.

Synthetic resins. These are tending to displace the natural products as additives and some of them are used as partial or complete substitutes for drying oils as vehicles.

In the first group are the epoxy, vinyl, melamine, phenolic, acrylic, and coumarone resins, some of which are of greater interest to the paint manufacturer although probably all have found uses in printing inks.

The most important of the second group are the phthalic acid derivatives known as alkyds. These are formed by the reaction between phthalic acid, usually as its anhydride, and a polyhydric alcohol. To present the subject in the simplest possible manner, ethylene glycol is selected:



Ethylene glycol Phthalic anhydride

The result of this condensation reaction is a linear alkyd polymer, but if glycerol is used in place of the glycol the product is a more resinous three-dimensional solid.

As a further step in the preparation of an oleoresinous polymer suitable as an ink (and paint) vehicle, one or more of the linseed oil fatty acids are caused to combine with the alkyd.

The polymer formed from the simpler action above may be set down as:

$$(-\ OCH_2CH_2O.COC_6H_4CO.OCH_2CH_2O.COC_6H_4CO.-)_n$$

Glycol — Phthalic anhydride — Glycol — Phthalic anhydride

Pigments. Although the words "pigment" and "dye" are often regarded as interchangeable, these materials are, in fact, very different; a pigment is a coloured insoluble or almost insoluble solid which is carried in a liquid or solid vehicle to which it imparts its colour, while a dye is a substance carried in a solvent which is fixed in or on a material, typically a textile. The colour of many dyes does not appear until after processing; for example indigo as applied to the fabric is colourless; the deep blue appears after exposure to air and light.

Most pigments are simple inorganic compounds often of mineral origin, while the great majority of dyes are organic and sometimes very complex.

The colouring materials of printing are almost wholly pigments but small quantities of dyes are sometimes added to inks with a volatile vehicle and a blue dye to news inks to counter the often rather brownish tone of the unsupported black.

In view of the very large range of pigments available, it is not possible in this work to consider more than a few of those in use.

Black. By far the greater part of the black pigment in use is carbon in a finely divided state. The most intense black is obtained by the controlled incomplete combustion of the gaseous and lighter liquid hydrocarbons. Lamp and vegetable black is the similar, but far less pure, product of the burning of waste from coal tars.

White. There are many white pigments, some of them rarely used in printing inks; however, those that find favour for the purpose are: titanium dioxide, TiO_2, a white of high opacity and almost certainly the best in its field; zinc oxide, ZnO; lithopone, a mixture of ZnS and $BaSO_4$; and alumina hydrate, $Al_2O_3x(H_2O)$.

Metallic chromates. The chromates of many metals are valuable pigments with a colour range from a pale yellow to red; among these are: normal lead chromate, $PbCrO_4$, a golden yellow; basic lead chromate, probably $PbO.PbCrO_4$, much deeper in colour than the former and tending to a red; lead chromate–sulphate, $PbCrO_4.PbSO_4$, a delicate lemon yellow; lead chromate-molybdate, $PbCrO_4.PbMoO_4$, a scarlet; and zinc chrome, probably $4ZnCrO_4.Zn(OH)_2$, a basic chromate and a pale yellow.

Prussian blue. This is a ferric-ferrous compound with prob-

able formula K_3Fe_4 $(Fe(CN)_6)_3$ which varies in colour according to the method of preparation from a rich royal blue to the delicate chinese blue with a hint of green.

Green. Many greens are prepared by the mixture of one of the blues above and a chrome yellow.

Cadmium yellow. This is a brilliant yellow, long valued for its stability and durability; its formula is CdS, i.e. cadmium sulphide.

Preparation of pigments. Many of the above may be made in the laboratory by adding to a solution of a soluble salt of the metal a solution of an alkali salt containing the required acidic radicle; thus if to a solution of cadmium nitrate, sodium sulphide is added, the pigment will be precipitated:

$$\underset{\text{Cadmium nitrate}}{Cd(NO_3)_2} + \underset{\text{Sodium sulphide}}{Na_2S} = \underset{\text{Sodium nitrate}}{2NaNO_3} + \underset{\text{Cadmium sulphide}}{CdS\downarrow}$$

Opacity of ink. For an ink to be as nearly opaque as possible the refractive indices (see Chapter 9) of ink and vehicle must be widely separated. This separation exists between boiled linseed oil and titanium dioxide with the result that an ink with these materials is of high opacity while if alumina hydrate is used the ink has so little opacity that it may be said to be almost transparent.

Ink Tests

There are many empirical tests of printing ink, the result of the accumulated experience of centuries; indeed, the application of the scientific method with its accompanying apparatus is often a means to prove quickly that which is already known to the experienced. The influence of viscosity upon printability was probably well known to Caxton, but the applied science of viscometry belongs to the near past.

In the matter below it is possible to suggest a few only of the increasing number of instrumental tests now becoming available.

Viscosity. Since viscosity is a general property of liquids, the subject is discussed in Chapter 6.

Light stability. It is all too apparent that many, if not most, colours fade in bright light, but natural conditions are of little use for testing the stability of colour on account of their irregularity or uncertainty. Systematic testing of solid patches of printing

ink (or paint) may be carried out by exposure for prolonged periods to a mercury vapour lamp, carbon arc, or xenon arc in a small enclosure which must be air-cooled. A control sample, shielded from the light, is necessary. This type of test is largely comparative; for example, two visually identical yellow inks, with pigments which differ chemically, are examined after exposure side by side but, in all cases, consideration must be given to possible changes in the colour of the vehicle or other components.

Colour correctness. It is probable that the efficiency of the really experienced colour-matcher cannot be achieved instrumentally, but supporting evidence is obtainable by the use of a sensitive spectrophotometer (see p. 118). It is imperative, however, that visual matching should take place under a standard illuminant, such as that of BS 950, 1967, and that consideration should be given to the possibility of metamerism, i.e. to the similarity in appearance of certain mixtures of pigments under illuminants with widely separated characteristics.

Drying time. Instrumental estimation of the drying time of an ink may be undertaken by the use of a turntable apparatus; the ink is applied by roller to three heavy glass discs which are rotated by a small motor with a reduction gear in such a manner that complete spiral traversal takes 24, 36, and 48 hr respectively (other periods are possible if needed). A small hopper moving from rim to centre at each disc trickles fine sand on the ink; the moment of drying is at that point on one or other of the discs where the sand ceases to stick.

Covering power. The opacity or covering power of an ink, particularly that of a coloured ink, may be assessed by imposing a band of the test colour across a bar in black ink on white paper; the extent to which the colour obscures the black is a criterion of its opacity, and the difference between a transparent and a more opaque ink is apparent. This test is not quantitative but it does offer comparative evidence.

Acid and alkali resistance. It is necessary for many packaging purposes that a printing ink should be chemically resistant. An ink may be tested for this quality by partially immersing strips of the dried ink on paper or board in dilute aqueous solutions of

strong and weak acids and alkalis, contained in large test tubes, for about an hour at the end of which the immersed portion may be compared with that outside the tube. The ink may be tested for its resistance to sulphur dioxide, SO_2, the bleaching agent present in the atmosphere of many industrial areas, by similar immersion in sulphurous acid, made by passing the dioxide into water.

Gloss. The gloss of a dry ink may be determined by the use of the apparatus employed for the same purpose for paper; it is however, desirable in order to minimize the influence of the paper that the latter should be uncoated and preferably of a dark colour.

Tests of drying oils. The most important of the properties of an oil intended as an ink vehicle are (a) the degree of unsaturation of its fatty acid, and (b) the character of that acid. These properties may be established by the normal practices of organic chemistry:

(i) Iodine of precise concentration in alcohol is trickled from a burette into a measured quantity of the oil; the iodine is accepted into the unsaturated positions, this being indicated by the discharge of its colour; when saturation is reached the iodine solution remains unaltered. The result of the test is expressed as the 'iodine value', i.e. the weight of iodine in grams which combines with 100 g of the oil.

(ii) In this practice the glycerol is detached from its oil by the use of an alkali to give a soap. An excess solution of potassium hydroxide of known concentration in alcohol is passed from a burette into a precise amount of the oil. When saponification is complete the unreacted alkali is determined by titration with an acid and using a phenolphthalein indicator. The result, the 'saponification number' or 'value', expresses the quantity of potassium hydroxide in milligrams needed to saponify 1 g of the oil.

CHAPTER 22

The Materials of Binding

Introduction. Papers, boards, and adhesives are all binding materials but they also have their uses in other sections of the industry and, as such, they are considered in earlier chapters. It is proposed here to examine briefly those materials which may be deemed to be particular to bookbinding; these include various leathers, the more or less successful substitutes for leather, cloths, and the metallic foils for blocking.

Leather. This is the binding material *de luxe* which, while widely used in the past, is now largely confined to limited editions of fine books, volumes privately bound for libraries and account books.

Leather is defined as the substance produced when animal skins are subjected to various processes during which the skins cease to be liable to putrescence. The processes are adapted to the purposes for which the final product is intended from the almost rigid sole leathers to the very supple materials used for gloves.

The initial treatment is much the same whatever the final product; the hair and the greater part of the epidermis—the outer layer—are removed by the caustic action of milk of lime, i.e. slaked lime, $Ca(OH)_2$, in water. Any residual unwanted material is disposed of by scraping to leave the true skin, the corium, which is a complex protein chemically related to gelatin.

The final process as far as leather properly so called is concerned, is tanning. The tannins or tannic acids are astringent substances of vegetable origin which occur in oak bark, gall nuts, and the leaves and wood of sumach, hemlock, and many other trees and plants.

Chemically, they are a group of compounds of which gallic acid, $C_6H_2(OH)_3COOH$, may be accepted as representative.

The tannins react with proteins in some manner apparently not fully understood to produce insoluble precipitates with the normally soluble albumin and gelatin and to give flexible leathers in which putrefaction is inhibited.

The most suitable bookbinding leathers are said to be those tanned with materials derived from sumach and various Mediterranean and American shrubs which also provide dyes and drugs.

Chrome tanning has replaced the vegetable derived process for many purposes particularly since it occupies very much less time. Chrome alum, $K_2SO_4 : Cr_2(SO_4)_3.24H_2O$, is the principal tanning agent, but sodium dichromate, $Na_2Cr_2O_7$, is much used, followed by sodium thiosulphate, $Na_2S_2O_3$, the photographers' hypo.

The leathers favoured for bookbinding are morocco from goatskin; russia from calf; basil, skiver, etc., from sheep skin, with pig and seal skin. Vellum also has some uses; this is a leather prepared basically for writing which has been employed for this purpose for many centuries.

Durability of leather. Observers have noted that the leather bindings of the last century are much more subject to decay than those of earlier times. This surprising information resulted in an inquiry during which it was shown that the cause is the presence of sulphuric and/or sulphurous acids in the leather or possibly of salts which hydrolyse to these acids. The origin of the acid materials is to be found in the atmosphere of industrial areas which is liable to carry substantial amounts of sulphur dioxide, SO_2, and to the use of acid dyes, many of which are associated with these acids or their salts. It is stated that the leather may be secured against these attacks by subjecting it to a dilute solution of potassium lactate, $CH_3CH(OH)COOK$.

A test to determine the resistance of leather to this acid-induced decay has been devised by the Printing Industry Research Association (PIRA). The sample is treated with dilute sulphuric acid and after air drying it is subjected to the powerful oxidizing agent, hydrogen peroxide, H_2O_2 for one treatment daily during a week; at the end of the test the sample is compared with the untreated

leather. It is claimed that this test is equal to a quarter of a century of exposure to a noxious atmosphere.

Cloth. This is the normal material of mass production binding or casing. Any of the familiar textiles will serve, but it is probable that linen is favoured for durability.

Leather cloth. It is rather unfortunate that many of these materials simulate leather at all since they possess admirable qualities in their own right. The first of these cloths was a textile more or less waterproofed with an oily substance and covered with a paint on which a pattern was impressed by rolling. The newer materials are much the same in character, but the surfaces are one or other of the many plastics applied in liquid form.

Tests of the stability of dyed materials. All the bindings and casings may be tested for the resistance of their dyes to chemically induced fading by immersion in dilute acids and alkalis in the manner outlined as similar tests for ink on p. 344; they may also be subjected to the same tests for stability in light.

Metallic foils. The remarkable malleability of gold and its almost total chemical inertia renders it the finest of all materials for blocking apart from its incomparable decorative qualities. Brass, with its copper content, and silver are subject to attack by sulphur which may be derived from compounds in the base or from airborne hydrogen sulphide. Tests for the possibility of the former may be undertaken by the method given in Chapter 20. Aluminium is relatively inert and when anodized is almost completely so (see Chapter 19); the anodized layer will accept dyes with charming decorative effects.

Attack by pests. The materials of bindings, particularly the leathers, are subject to the attacks of insects and rodents; the former include cockroaches and, more traditionally, bookworms which are the larvae of several species of beetles. Insecticides sprinkled on the shelves will assist in repelling the smaller creatures. Rats and mice enjoy the adhesives rather than the bindings themselves; while these pests may be fairly effectively controlled by chemical means, some of the materials containing the very controversial phosphorus, there are also the well-established technologies of traps and cats.

CHAPTER 23

Adhesives

Introduction. Adhesives must have been known long before recorded history since they are far from scarce and even abundant in some forest regions as the gums and resins exuded from many trees, while their sticky properties are very evident.

Although adhesion is well known in woodworking, paper and board converting and the textile industries among the many, it may be seen as rather surprising that so little was understood about the action of adhesion until quite recently; indeed, the growth of knowledge in the subject was largely the result of the needs of the Second World War when adhesives were developed capable of bonding metals and other materials previously supposed almost unstickable.

It is now apparent that there are several manners of adhesion, but these may be reduced to two for the present purpose. When two surfaces such as those of uncoated paper or board are treated with a gum and pressed into contact with the lapse of more or less time, the materials are separable with difficulty if at all; it may be accepted that the gum has penetrated the interstices between the fibres of the paper or board and, in solidifying by the evaporation and escape of any solvent, a bonding is created. This type of adhesion has been called mechanical bonding.

When a thin metal or glass rod is broken by bending, considerable force must often be exerted, but if tension is applied in the direction of the rod a very much greater effort is necessary to disrupt the internal cohesive forces. In either case, assuming a

clean fracture, it is reasonable to wonder why, if the pieces are replaced in close contact, the cohesion is not resumed; there appears to be no simple answer to this question.

But in the second type of adhesion, using adhesives which differ chemically from the gum, intermolecular cohesive forces actually appear to be formed; these adhesives are believed to react chemically with the materials of the surfaces to which they are applied with the effect that, after pressure contact and time to set, the intermolecular forces between surface and surface through the bonding are frequently as effective, and sometimes more effective, than those of the materials themselves. This form of adhesion is usually called chemical bonding.

Adhesives—general. What are commonly known as natural adhesives are either of vegetable origin, the gums and resins, or are animal products such as the glues.

Almost all the synthetic materials are also called resins since, although they are very different in chemical composition, their properties resemble those of nature in many respects. The synthetics are polymers which may be subjected to further stages of polymerization during setting.

It will be appropriate here to give definitions of "gum" and "resin":

A gum is a water soluble or miscible material usually colloidal in character.

A resin is a substance soluble in organic solvents with little or no aqueous solubility.

Properties for printing and bookbinding. For the purposes of these industries an adhesive must possess considerable flexibility and its pH value should conform closely to that of the adherends—the materials to be stuck—since wide, or even not so wide, differences in acidity or alkalinity may result in fading, if not destruction, of the colouring matters of paper, board, and leather while these materials may themselves be attacked. Further, since paper, board, and leather are all derived from living substances, the adhesives should be sterile and, as far as possible, not themselves liable to be attacked by micro-organisms.

Wetting agents. Differences in surface tension between adherend and adhesive may prevent the latter from wetting the former with the result that adhesion is weakened or, in extreme cases, inhibited. It is therefore necessary to adjust the surface tension of the adhesive, since that of the adherends cannot be adjusted by the addition of a wetting agent or surfactant.

To wet as here understood has a meaning beyond that in ordinary usage; the liquid, whatever its character, should flow at once over the adherend and the contact established should be permanent; to state this in other terms, adhesive and adherend must not be mutually repellent.

A wetting agent has the property of tending to concentrate at the liquid–solid (or, for other purposes, the liquid–air) interfaces since their molecules possess affinities with both components.

The best-known wetting agents are the sodium salts of the intermediate to the higher fatty acids, and they are thus, by definition, soaps; an example which will typify the many is sodium laurate, $C_{11}H_{23}COONa$. Among others are amine salts such as methylamine hydrochloride, $CN_3NH_2.HCl$; sulphonic acid derivatives of oils—these have the acid group, $-SO_2OH$, and esters (and polyesters) of fatty acids such as butyl stearate, $CH_3(CH_2)_{16}COO(CH_2)_3CH_3$.

Viscosity of adhesives. The majority of the adherends of printing and book binding are more or less porous and absorbent and therefore, while the adhesive must be freely accepted at the surfaces, its viscosity should not be so low that too much is absorbed too quickly. Viscosity generally decreases with rising temperature and consequently, with those adhesives which are applied hot, a balance between viscosity and temperature must be established.

A CLASSIFICATION OF ADHESIVES

(a) **Vegetable adhesives.** These are by far the most widely used of all the available materials. The majority of them may be described as water soluble thermoplastics; the water solubility remains unless they are treated chemically to create thermosetting plastics

by full three-dimensional polymerization. These adhesives set primarily by removal of their water by evaporation.

(i) *Starch.* Rice, wheat, and potatoes are all sources of starch but for adhesives that derived from maize (corn in North America) is of the greatest importance.

In the manufacture of starch from maize, the grains are treated with warm sulphurous acid, H_2SO_3, made by passing sulphur dioxide, SO_2, into water; the grains are crushed and the oily matter removed. The fibrous and other materials unwanted for the purpose are separated centrifugally to leave the residual starch.

Chemically starch is a carbohydrate of the polysaccharide type and it is thus closely related to the sugars and to cellulose. Its empirical formula is $(C_{12}H_{20}O_{10})_n$, where n is a very high number and thus the molecule of starch is of large molecular weight.

(ii) *Dextrine.* When dry starch is subjected to a temperature of about 250° C the structure is partially degraded or simplified to give a cold-water soluble dextrine sometimes known as British gum, while its syrupy solution in water is mucilage.

(iii) *Gums.* Gum-arabic may be accepted as typifying the gums of vegetable origin. Since this material is almost indispensable in the lithographic process in general and it is an important constituent of the light-sensitive coating in deep-etch platemaking, the reader is referred to Chapters 16 and 19 for discussion of the subject.

(b) **Animal adhesives.** These resemble most of the vegetable adhesives in being water soluble and they set in the same manner. However, since many of them are chemically close to gelatin, their warm solutions tend to gel on cooling.

(i) *Glues.* These are derived mainly from the collagen of bones and hides and their character varies considerably according to the source. The process for the extraction of the crude glue is essentially one of prolonged boiling of the raw materials.

Glues are proteins with a molecule built up of twenty or more amino acids and they are consequently among the most complex of all organic substances; it is, indeed, impossible to represent glue or any other protein in a simple manner.

Fish-glue is an important material for providing the image on

metal in the photoengraving process and it is also considered in Chapter 16.

(ii) *Casein.* This adhesive is prepared from milk in which it occurs as the calcium salt. It is manufactured by treating warm, skimmed milk with lactic or mineral acids; the resulting precipitate is crude casein. Casein is also a complex protein which yields phosphoric acid when suitably treated and it is often called a 'phosphoprotein' in consequence.

(c) **Synthetic resins.** Many of these materials used as the vehicles or additives of printing inks are also used as adhesives in liquid form or as solutions in organic solvents. The reader is therefore referred to Chapter 21 for further information.

Index

Notes:

(a) Where the same words are used variously they are differentiated by bracketed explanatory terms.

(b) The abbreviations used are: (alg.) algebra; (arith.) arithmetic; (BS) British Standard; (chem.) chemistry; (elec.) electricity; (electrodep.) electrodeposition; (geom.) geometry; (litho.) lithography; (photo.) photography; (phys.) physical; (print.) printing.

(c) Only elements and compounds of major printing importance are shown.

(d) The coded references of figures and tables are cited in the appropriate matter.

(e) The page numbers refer to the beginning of the subject; where more than one number is shown the subject appears under more than one heading.

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